

CHEMICAL MODIFICATIONS OF
POLYMER-DERIVED SILICON CARBIDE FIBERS
TO ENHANCE THERMOMECHANICAL STABILITY

BY
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To My Family

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TABLE OF CONTENTS

	page
ACKNOWLEDGEMENT	iii
LIST OF TABLES	vi
LIST OF FIGURES	ix
LIST OF ABBREVIATIONS	xiv
ABSTRACT	xvii
CHAPTERS	
1. INTRODUCTION	1
2. LITERATURE SURVEY	8
Ceramic Matrix Composites	8
Mechanical Behavior of Ceramic Fibers	14
Evolution of SiC Fibers	18
Nicalon and UF SiC Fibers	22
Polymer Precursors for SiC Materials	26
Characterization of SiC Materials	33
Preparation of Si and SiC Particles	43
Carbides and Silicides	47
Densification Behavior of SiC	48
Boron Precursors	59
3. EXPERIMENTAL PROCEDURE	67
Preliminary Study 1: Polymerization and Copolymerization	67
Preliminary Study 2: Carbide Formation Reactions	71
Preliminary Study 3: Decaborane High-dope Study	73
Fibers from PCS-based Polymers	76

Fibers from PCS-based Polymers with Decaborane	82
Fibers from PCS-based Polymers with Si Particles	87
Fibers from PCS-based Polymers with Si Particles and Decaborane	92
Other Fibers	94
Fibers from PCS-SX Polymers	94
Fibers from PCS-SZ Polymers with SiC Particles	94
Characterization	96
 4. RESULTS AND DISCUSSION	 102
Preliminary Study 1: Polymerization and Copolymerization	102
Preliminary Study 2: Carbide Formation Reactions	105
Preliminary Study 3: Decaborane High-dope Study	120
Fibers from PCS-based Polymers	136
Fibers from PCS-based Polymers with Decaborane	146
Fibers from PCS-based Polymers with Si Particles	183
Fibers from PCS-based Polymers with Si Particles and Decaborane	206
Fibers from PCS-SX Polymers	225
Fibers from PCS-SZ Polymers with SiC Particles	230
 5. CONCLUSIONS	 236
 6. FUTURE WORK/SUGGESTIONS	 240
 REFERENCES	 242
 BIOGRAPHICAL SKETCH	 260

LIST OF TABLES

	page
1.1 Properties of Commercial Ceramic Fibers	2
1.2 Properties of Silicon Carbide Materials	4
2.1 Potential Markets of Ceramic Composite Materials	10
2.2 Research Programs for Ceramic Composite Materials in USA	13
2.3 Summarized Properties of Selected Carbide Materials	50
2.4 Properties of Potential Silicide Materials	54
2.5 List of Potential Boron Precursors	63
3.1 List of Studied Chemical Reagents	68
3.2 Properties of Dow Corning Polycarbosilane	69
3.3 List of Silicide Particles for Carbide Reaction Study	72
3.4 Polymer Compositions in Carbide Reaction Study	72
3.5 Polymer Compositions in Decaborane High-dope Study	77
3.6 Summarized Compositions and Processing of CP Fiber Batches (PCS-base polymer)	79
3.7 Summarized Compositions and Processing of CPD Fiber Batches (PCS-based polymer + decaborane)	83
3.8 Summarized Compositions and Processing of CS Fiber Batches (PCS-based polymer + Si particles)	88
3.9 Summarized Compositions and Processing of CSD Fiber Batches (PCS-based polymer + Si particles + decaborane)	93

3.10	Summarized Compositions and Processing of CY Fiber Batches (DC PCS-SX polymer with/without decaborane)	95
3.11	Summarized Compositions and Processing of CX Fiber Batches (DC PCS-SZ polymer + SiC particles)	95
4.1	Summarized Results of Ceramic Yield Measurements: after 1000°C Pyrolysis	121
4.2	Summarized XPS Results: Atomic Concentration for Pyrolyzed Disks	132
4.3	Summarized XPS Results: Binding Energy and FWHM	134
4.4	XPS Peak Positions in Literatures	135
4.5	Tensile Properties of CP Fibers (PCS)	137
4.6	Tensile Properties of CPD Fibers (DC PCS-SZ + decaborane): CPD1 to CPD8	149
4.7	Tensile Properties of CPD Fibers (DC PCS-SZ + decaborane): CPD9 to CPD11	151
4.8	Tensile Properties of CPD13 and CPD14 Fibers (DC PCS-SZ + decaborane + DPEA): Effect of Spinning Atmosphere	158
4.9	Tensile Property Comparison: Effect of Decaborane Incorporation	158
4.10	Summarized Properties of Dow Corning New SiC Fibers	162
4.11	Tensile Property Comparison: Effect of Decaborane Content	164
4.12	Tensile Property Comparison: Effect of Soaking in Decaborane Solution	167
4.13	Summarized XRD Results: Effect of Decaborane Incorporation on Crystallinity after 1800°C Treatment	178
4.14	Measured Density of SiC Fibers after Pyrolysis and after 1800°C Treatment: Effect of Decaborane Incorporation	182
4.15	Tensile Properties of CS Fibers (DC PCS-SZ + Si): CS1 to CS11	188

4.16	Summarized XRD Results of CP5 (DC PCS-SZ) and CS9 (DC PCS-SZ + Si) Fibers: Effect of Si Particle Incorporation on Crystallinity after Heat-treatments	193
4.17	Tensile Properties of CS Fibers (UF PCS-PSZ + Si): CS12 to CS14	199
4.18	Summarized Results of Neutron Activation Analysis	205
4.19	Measured Density of CS14 Fibers (UF PCS-PSZ + 25 w/o Si)	207
4.20	Summarized Results of BET Analysis of CS Fibers (PCS + Si)	207
4.21	Tensile Properties of CSD Fibers (PCS + Si + decaborane)	210
4.22	Weibull Moduli of Selected CP (PCS), CPD (PCS + decaborane), CS (PCS + Si) and CSD (PCS + Si + decaborane) Fibers	220
4.23	Tensile Properties of CY Fibers (DC PCS-SX with/without decaborane)	227
4.24	Tensile Properties of CX Fibers (DC PCS-SZ + SiC)	232

LIST OF FIGURES

	page
1.1 SiC Fiber Processes of (a) Nicalon and (b) UF Fibers	5
2.1 Schematic Morphology of a Typical Fracture Cross-section of Brittle Materials	15
2.2 A Typical Weibull Plot: UF 127-12 SiC Fibers	19
2.3 Tensile Strengths of UF and Nicalon SiC Fibers: Effect of Heat-treatment .	24
2.4 A Schematic Structure of Branched Polycarbosilane	29
2.5 Melting Temperatures of Binary Refractory Materials	49
2.6 Chemical Structure of Decaborane ($B_{10}H_{14}$)	64
2.7 Chemical Reaction Tree of Decaborane ($B_{10}H_{14}$)	66
3.1 Temperature Profiles of 1000°C Pyrolysis	74
3.2 Temperature Profiles of Heat-treatments	75
3.3 SEM Micrographs of Spinneret Holes: (a) 4-hole and (b) 8-hole Spinneret . .	81
3.4 Flow Diagram of CS Fiber Processing	90
3.5 Schematic Diagram of Fiber Specimen for Tensile Testing	97
4.1 Composition Diagram of Silazane Polymerization	103
4.2 Composition Diagram of Siloxane Polymerization	104
4.3 Composition Diagram of DC PCS-Silazane Copolymerization	106

4.4	X-ray Diffraction Patterns of PCS-SZ Copolymer: Effect of Heat-treatment Temperature (a) before Pyrolysis, (b) after 1300°C Treatment, (c) after 1400°C Treatment and (d) after 1500°C Treatment	107
4.5	X-ray Diffraction Patterns of a Mixture of PCS-SZ Polymer and Si Particles: Effect of Heat-treatment Temperature (a) before Pyrolysis, (b) after 1300°C Treatment, (c) after 1400°C Treatment and (d) after 1500°C Treatment	109
4.6	X-ray Diffraction Patterns of a Mixture of PCS-SZ Polymer and Si Particles: Effect of Temperature Profile during 1400°C Treatment (a) with no hold at 1000°C and (b) with one hour hold at 1000°C	111
4.7	HT-XRD Peak Intensity Change of a Mixture of PCS-SZ Polymer and Si Particles	112
4.8	X-ray Diffraction Patterns of a Mixture of PCS-SZ Polymer and HfSi ₂ : Effect of Heat-treatment Temperature (a) before Pyrolysis, (b) after 1300°C Treatment and (c) after 1500°C Treatment	114
4.9	HT-XRD Peak Intensity Change of a Mixture of PCS-SZ Polymer and HfSi ₂ Particles	116
4.10	X-ray Diffraction Patterns of a Mixture of PCS-SZ Polymer and TiSi ₂ : Effect of Heat-treatment Temperature (a) before Pyrolysis and (b) after 1500°C Treatment	117
4.11	HT-XRD Peak Intensity Change of a Mixture of PCS-SZ Polymer and TiSi ₂ Particles	119
4.12	TG/DTA Results of Decaborane to 1000°C: (a) Regular Pyrolysis Temperature Profile and (b) Fast Pyrolysis Temperature Profile	122
4.13	SEM Micrographs of Pyrolyzed Decaborane High-dope Disks: (a) without Decaborane and (b) with Decaborane (15 w/o)	125
4.14	X-ray Diffraction Pattern of As-purchased Decaborane	126
4.15	X-ray Diffraction Patterns of (a) PCS-SX polymer and (b) Decaborane High-dope PCS-SX Polymer, before and after 1000°C Pyrolysis	127
4.16	X-ray Diffraction Patterns of (a) PCS-SZ Polymer and (b) Decaborane High-dope PCS-SZ Polymer, before and after 1000°C Pyrolysis	129

4.17	XPS Wide Scan Spectrum of Pyrolyzed Disk: Decaborane High-dope PCS-SX Polymer	130
4.18	XPS Wide Scan Spectrum of Pyrolyzed Disk: Decaborane High-dope PCS-SZ Polymer	131
4.19	SEM Micrographs of As-pyrolyzed CP4 Fibers (DC PCS-SZ): (a) Surface and (b) Cross-section	141
4.20	X-ray Diffraction Patterns of CP5 Fibers (DC PCS-SZ): Effect of Heat-treatment Temperature (a) after Pyrolysis, (b) after 1300°C Treatment, (c) after 1400°C Treatment and (d) after 1500°C Treatment	145
4.21	SEM Micrographs of CPk Fibers (UF PCS-PSZ): (a) As-pyrolyzed and (b) after 1800°C Treatment	153
4.22	SEM Micrographs of (a) CPD9A and (b) CPD10A Fibers (DC PCS-SZ + 1.5 w/o decaborane) after 1800°C Treatment: Effect of SZ Content on Surface Morphology	154
4.23	SEM Micrographs of CPD17 Fibers (UF PCS + 3.2 w/o decaborane): (a) As-pyrolyzed and (b) after 1800°C Treatment	160
4.24	SEM Micrographs of (a) CPD19 (1.1 w/o decaborane) and (b) CPD21 Fibers (7.5 w/o decaborane) after 1800°C Treatment: Effect of Decaborane Content on Surface Morphology	165
4.25	SEM Micrographs of (a) CP13P Fibers (UF PCS), (b) CP13P after 1800°C Treatment (c) CP13 after 1800°C Treatment and (d) CP13D Fibers (soaked in decaborane solution) after 1800°C Treatment	169
4.26	SEM Micrographs of CPD23F Fibers (3.1 w/o decaborane with fast heating): (a) Rough Surface and (b) Smooth Surface after 1800°C Treatment	171
4.27	SEM Micrographs of (a) CPD24F (3.2 w/o decaborane) and (b) CPD24FD Fibers (soaked in decaborane solution) after 1800°C Treatment: Effect of Soaking in Decaborane Solution on Surface Morphology	172
4.28	X-ray Diffraction Patterns of CP13-18 and CPD24F Fibers: Effect of Soaking in Decaborane Solution after 1800°C Treatment (a) CP13, (b) CP13 with Soaking, (c) CPD24F and (d) CPD24F Fibers with Soaking	173

4.29	SEM Micrographs of Surfaces of (a) CP14 (UF PCS), (b) CP14N (soaked in decaborane-SZ solution), (c) CP14M (soaked in decaborane-PSZ solution) and cross-section of (d) CP14M Fibers after 1800°C Treatment	176
4.30	Plot of XRD Peak Area versus Crystallite Size: CP (PCS) and CPD (PCS + decaborane) Fiber Batches after 1800°C Treatment	180
4.31	Plot of Elastic Modulus versus Crystallite Size: CP (PCS) and CPD (PCS + decaborane) Fiber Batches after 1800°C Treatment	181
4.32	Particle Size Distribution of (a) As-received and (b) Fractionated Si Particles .	184
4.33	SEM Micrographs of As-pyrolyzed CS5 Fibers (DC PCS-SZ + 14 w/o Si): (a) Surface and (b) Cross-section	186
4.34	Tensile Strength and Elastic Modulus of CP (PCS) and CS (PCS + Si) Fiber Batches after 1000°C Pyrolysis	191
4.35	X-ray Diffraction Patterns of CS9 Fibers(DC PCS-SZ + 14 w/o Si): Effect of Heat-treatment Temperature (a) As-pyrolyzed, (b) after 1300°C Treatment, (c) after 1400°C Treatment and (d) after 1500°C Treatment	192
4.36	TEM Micrographs of CS3 Fibers (DC PCS-SZ + 14 w/o Si): (a) Bright Field Image and (b) Electron Diffraction Pattern after Pyrolysis, (c) Bright Field Image and (d) Electron Diffraction Pattern after 1300°C Treatment	195
4.37	Auger Electron Spectra of (a) CP6 (PCS) and (b) CS14 fibers (PCS + 25 w/o Si) after 1000°C Pyrolysis	197
4.38	X-ray Diffraction Patterns of CS14 Fibers: Effect of Heat-treatment Temperature (a) As-pyrolyzed, (b) after 1200°C Treatment, (c) after 1300°C Treatment and (d) after 1500°C Treatment	200
4.39	SEM Micrographs of CS11 Fibers (DC PCS-SZ + 14 w/o Si): (a) As-pyrolyzed and (b) after 1800°C Treatment	201
4.40	SEM Micrographs of CS14 Fibers (UF PCS-PSZ + 25 w/o Si): (a) As-pyrolyzed and (b) after 1800°C Treatment	202
4.41	SEM Micrographs of HF-washed CS8 Fibers (DC PCS-SZ + 14 w/o Si): (a) As-washed and (b) after 1500°C Treatment	208
4.42	SEM Micrographs of CSD17 Fibers (DC PCS-SZ + 14 w/o Si + 1.6 w/o decaborane) : (a) As-pyrolyzed and (b) after 1800°C Treatment	211

4.43	SEM Micrographs of (a) CSD19 (UF PCS + 17 w/o Si + 2.7 w/o decaborane) and (b) CSD20 Fibers (UF PCS + 17 w/o Si + 6.4 w/o decaborane) after 1800°C Treatment: Effect of Decaborane Content on Surface Morphology . .	213
4.44	SEM Micrographs of (a) CSD21 (UF PCS + 17 w/o Si + 6.6 w/o decaborane) and (b) CSD21F Fibers (fast pyrolysis) after 1800°C Treatment: Effect of Fast Pyrolysis on Surface Morphology	215
4.45	Tensile Strength and Elastic Modulus of CPD (PCS + decaborane) and CSD (PCS + Si + decaborane) Fiber Batches after 1000°C Pyrolysis	216
4.46	Tensile Strength and Elastic Modulus of CPD (PCS + decaborane) and CSD (PCS + Si + decaborane) Fiber Batches after 1800°C Treatment	217
4.47	Plot of XRD Peak Area versus Fiber Elastic Modulus after 1800°C Treatment	219
4.48	Weibull Plot of CPk (UF PCS-PSZ) and CPk-18 Fibers	222
4.49	Weibull Plot of CPD22 (UF PCS + 3.4 w/o decaborane) and CPD22-18 Fibers	223
4.50	Weibull Plot of CSD21 (UF PCS + 17 w/o Si + 6.6 w/o decaborane) and CSD21-18 Fibers	224
4.51	SEM Micrographs of CY1 Fibers (DC PCS-SX + 1.5 w/o decaborane): (a) As-pyrolyzed and (b) after 1800°C Treatment	228
4.52	X-ray Diffraction Patterns of CY Fibers (DC PCS-SX with/without decaborane): (a) As-pyrolyzed, (b) after 1500°C Treatment and (c) after 1800°C Treatment	229
4.53	Auger Electron Spectrum of As-pyrolyzed CY1 (DC PCS-SX + 1.5 w/o decaborane) Fibers	231
4.54	SEM Micrographs of CX1 Fibers (DC PCS-SZ + 30 w/o SiC): (a) As-pyrolyzed and (b) after 1500°C Treatment	234
4.55	X-ray Diffraction Patterns of CX1 Fibers (DC PCS-SZ + 30 w/o SiC): Effect of Heat-treatment Temperature (a) As-pyrolyzed, (b) after 1200°C Treatment, (c) after 1500°C Treatment and (d) As-received α -SiC Particles	235

LIST OF ABBREVIATIONS

CP fibers	fibers derived from PCS-based polymers
CP#M fibers	M denotes that these CP fibers were soaked in SZ-DB solution for 12 hours
CP#N fibers	N denotes that these CP fibers were soaked in PSZ-DB solution for 12 hours
CP#NS fibers	NS denotes that these CP fibers were soaked in PSZ-DB solution for a short time (20 minutes)
CPD fibers	fibers derived from PCS-based polymers with decaborane
CS fibers	fibers derived from PCS-based polymers with Si particles
CSD fibers	fibers derived from PCS-based polymers with Si particles and decaborane
CSD#F fibers	F denotes a fast pyrolysis; two hours from 30 to 1000°C
CX fibers	fibers derived from PCS-based polymers with SiC particles
CY fibers	fibers derived from DC PCS-SX polymers with/without decaborane
DCP	dicumyl peroxide, free radical initiator
DC PCS	Dow Corning polycarbosilane
DC PCS-SX	copolymers of Dow Corning PCS and siloxane monomer
DC PCS-SZ	copolymers of Dow Corning PCS and silazane monomer
DC SiC fiber	SiC fibers newly developed at Dow Corning
DB	decaborane

DPEA	N, N-diisopropyl-ethylamine
EDS	energy dispersive spectroscopy
EM	elastic modulus; Young's modulus
EMP	electron microprobe
FP	fast pyrolysis (temperature profile)
FWHM	full-width-at-half-maximum (of a peak)
GPa	giga (10^9) pascal (N/m ²)
GPC	gel permeation chromatography
HT-XRD	XRD instrumentation with a hot stage
JCPDS	joint committee of powder diffraction society
MW	molecular weight
NAA	neutron activation
PCS	polycarbosilane
PIB	polyisobutylene
PSZ	polysilazane
RP	regular pyrolysis (temperature profile)
RS	rupture strain; strain at break
RT-XRD	XRD instrumentation without a hot stage
SAM	scanning Auger microscopy, also known as Auger electron spectroscopy (AES)
SEM	scanning electron microscopy
SX	siloxane monomer
SZ	silazane monomer

TEM	transmission electron microscopy
TG/DTA	thermogravimetric/differential thermal analysis
TS	tensile strength
UF PCS	PCS synthesized at University of Florida
WDS	wavelength dispersive spectroscopy
w/o	weight per cent
XRD	x-ray diffractometry

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Low-oxygen SiC fibers of a good thermostability were developed at the University of Florida. Those fibers turned out to have a significant level of excess carbon, which led to low elastic modulus and low thermal stability relative to SiC. Two approaches were studied to improve the stoichiometry and the thermostability of SiC fibers: Si particle incorporation and decaborane incorporation. In preliminary studies, it was found that Si, HfSi_2 and TiSi_2 particles reacted with excess carbon in polymer-derived SiC structure during heat-treatments and created additional carbides. Carbothermal reactions proceeded greatly at temperatures much lower than their melting temperatures. Also it was found that the decaborane could work as a boron-releasing densification aid.

Studied SiC fibers are classified into four major categories: CP fibers; CPD fibers (with decaborane); CS fibers (with Si particles); and CSD fibers (with Si particles and

decaborane). CP fibers, irrespective of compositions, became fragile after 1500°C heat-treatment whereas they were good up to 1400°C heat-treatment. Boron incorporation remarkably enhanced the thermomechanical stability of fibers. Surfaces of CPD fibers remained rather dense and more clean even after 1800°C treatment. Decaborane incorporation assisted the crystallization process in fibers during 1800°C treatment and greatly increased the elastic modulus of fibers.

Silicon particles incorporation resulted in improved fiber stoichiometry of silicon to carbon. However, the thermomechanical stability of fibers was not improved by Si incorporation. Porous microstructure resulted even after 1300°C treatment. This was probably due to two factors: oxidation by Si particles and volume shrinkage by carbothermal reduction reactions. Decaborane incorporation to CS fibers improved the thermomechanical stability to a great extent. Though CSD fibers had rough surfaces after 1800°C treatment, their strength retention was as high as 70%. Elastic modulus as high as 300 GPa was attained by a batch of CSD fibers. Additionally, CSD fibers had fiber density as high as 2.92 g/cm³ after 1800°C treatment.

Fibers with good tensile properties were not obtained from siloxane-based copolymers with/without decaborane. α -SiC particle incorporated SiC fibers had good as-pyrolyzed tensile properties, but poor thermomechanical stability up to 1500°C due to surface oxidation.

CHAPTER 1 INTRODUCTION

The need for high-temperature structural materials for devices such as energy exchange systems, gas turbine engines and supersonic vehicles has provoked an enormous interest in ceramic materials. The advantages of ceramic materials in the gas turbine engine over metals would be higher operating temperature, reduced weight, increased efficiency and improved thrust-to-weight ratio. Ceramic materials, however, suffer from several problems: low fracture toughness, poor creep resistance, predicted low reliability and susceptibility to crack growth, which could cause catastrophic failure during operation.

Those problems have been solved to a great extent by introducing the concept of fiber-reinforced ceramic-matrix-composite (CMC). The fracture toughness and the reliability of CMC materials are much greater than those of monolithic ceramic materials. A variety of aspects of CMC materials have been and are being studied (Cao90, Car92, Gia91, Ho92, Mas85, Mec89, Pre89, She89, She92, Weh91, Yax93). Another important advantage of CMC materials is that the desired properties or performance of CMC's cannot be attained by monolithic materials.

Generally the performance of CMC materials strongly depends upon the properties of the reinforcing ceramic fibers. Ceramic fibers can be divided into two categories: oxide and non-oxide. Oxide fibers are represented by alumina and mullite

Table 1.1 Properties of Commercial Ceramic Fibers (Gal89)

manufacturer	designation	compositions	tensile strength (GPa)	elastic modulus (GPa)	density (g/cm ³)	diameter (μ m)
Textron	SCS-6	SiC(CVD) on C core	3.92	406	3.2	143
Textron	boron	B	3.5	413	3.0	140
Dow Corning	MPDZ	SiC _{1.46} O _{3.30} N _{0.64}	1.75-2.10	175-210	2.3	10-15
	HPZ	SiC _{3.40} O _{3.08} N _{0.95}	2.10-2.45	140-175	2.35	10
	MPS	SiC _{1.17} O _{3.03}	1.05-1.40	175-210	2.65	10-15
DuPont	FP	α -Al ₂ O ₃	1.40	385	3.9	20
	PRD-166	80% Al ₂ O ₃ /20% ZrO ₂	2.10-2.45	385	4.2	20
Nippon Carbon	Nicalon	SiC _{1.23} O _{3.30}	2.52-3.29	182-210	2.55	10-20
Sumimoto	Alumina	85% Al ₂ O ₃ /15% SiO ₂	1.80-2.60	210-250	3.2	9-12
3M	Nextel 312	62% Al ₂ O ₃ /14% B ₂ O ₃ /24% SiO ₂	1.75	154	2.7	11
	Nextel 480	70% Al ₂ O ₃ /28% ZrO ₂ /2% B ₂ O ₃	2.28	224	3.05	10-12
Ube	Tyramo	Si-Ti-C-O	2.97	200	2.4	8-10
Carborundum		BN	0.3-1.4	28-69	1.9	10
Tateho	whisker	Si ₃ N ₄	--	--	3.18	--

($\text{Al}_2\text{O}_3/\text{SiO}_2$) fibers, while the nonoxides consist of carbides, borides, nitrides and so forth. The most widely used nonoxide fibers are carbon, SiC, TiB_2 and Si_3N_4 . Table 1.1 summarizes commercial ceramic fibers with some of their properties.

Among all ceramic materials, silicon carbide (SiC) has been one of the most widely studied materials. The most advantageous features of SiC are low density, almost covalent bonding, low reactivity, high creep resistance and high melting point. There are currently many applications which use SiC materials not only for the matrix materials but also for the reinforcing fibers. Table 1.2 summarizes some physical properties of SiC materials.

Ceramic fibers are produced by various methods. The most well-known routes are sol-gel technology and preceramic polymer technology. The sol-gel method has been used to make oxide ceramic fibers while the polymer precursor route has been widely used to prepare non-oxide ceramic fibers. Currently there are two commercialized methods to produce SiC fiber: by spinning of melted SiC powder and by pyrolysis of preceramic polymer fibers to form SiC. The latter method has produced SiC fibers of the best overall performance and highest productivity. Polycarbosilane (PCS) and polysilane (PS) are the most widely used polymer precursors for SiC fiber.

PCS was first synthesized from polymethylsilane by Yajima et al. (Yaj75) via a high pressure conversion reaction. The PCS was melt-spun to make fibers and crosslinked at 200°C in air to avoid melting during the subsequent pyrolysis process. Later this method was commercialized in Japan to manufacture Nicalon^R SiC fiber. Figure 1.1(a) shows a flow diagram for the approximate Nicalon^R fiber process. Due to

Table 1.2 Properties of Silicon Carbide Materials

Description	Property
crystal structure	α (hexagonal) β (cubic)
theoretical density (g/cm^3)	3.21
Knoop hardness (GPa)	20 - 30
Poisson's ratio	0.19
thermal expansion ($\times 10^{-6} \text{ } ^\circ\text{K}^{-1}$)	4.3 - 5.6
thermal conductivity ($\text{W}/\text{m} \cdot ^\circ\text{K}$)	66-155 at 400°K 21-33 at 1400°K
specific heat ($\text{J}/\text{Kg} \cdot ^\circ\text{K}$)	628 - 1046
emittance	0.85 at 400°K 0.80 at 800°K
thermal shock resistance parameter	31

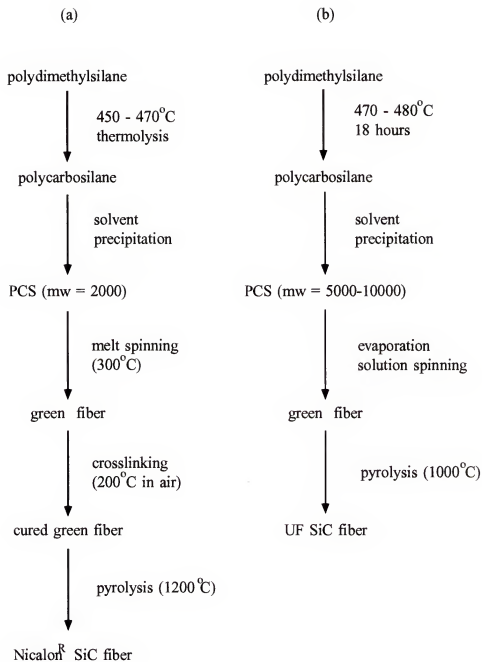
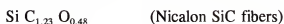


Figure 1.1 SiC Fiber Processes of (a) Nicalon and (b) UF fibers

the oxidative crosslinking in a Nicalon^R fiber process, even the best grade (ceramic grade) of Nicalon^R fibers contains a high level of oxygen. The high oxygen content (up to 15 w/o) in Nicalon^R fibers causes extremely low thermomechanical stability over 1300°C.

The need of oxidative crosslinking in the Nicalon^R fiber process was eliminated by a process developed at the University of Florida using PCS with a higher molecular weight (MW) and by including some additives. PCS of higher MW ($M_p = 5000-10000$) was synthesized at UF by Toreki and Batich in 1989 (Tore90). High MW PCS is not melted by heating but is soluble in some solvents such as toluene, which enabled us to make fibers via a solution spinning. A spinning aid and polysilazane (PSZ) were added to the polymer solution for enhanced spinning as well as for stability during pyrolysis. Since no oxidative crosslinking process was needed in the UF SiC fiber process, the oxygen content was much lower than that of Nicalon fiber. Figure 1.1(b) illustrates the UF SiC fiber process. The low oxygen content of UF SiC fiber enhanced thermomechanical stability at elevated temperatures.

Even though UF SiC fibers have low oxygen content, they turned out to have high carbon content compared to the stoichiometric SiC. Approximate chemical formulae, measured via a neutron activation analysis technique, of as-pyrolyzed UF SiC fibers and of as-received Nicalon^R SiC fibers are:



The high level of excess carbon resulted in a low crystallinity, after 1000°C pyrolysis under nitrogen, which subsequently resulted in a low elastic modulus. SiC fibers with well-controlled crystalline structure, such as Textron's SCS-series processed via chemical vapor deposition (CVD), can have an elastic modulus up to 400 GPa. Comparing SCS fibers with UF SiC fibers (up to 250 GPa), a stoichiometric modification method would be indispensable for an enhanced elastic modulus for the UF fibers.

Several different approaches to modify the stoichiometry in UF SiC fiber have been studied separately at UF. Addition of fine silicon particles to the PCS-based polymers has been studied and presented in this dissertation.

CHAPTER 2 LITERATURE SURVEY

Ceramic Matrix Composites

Approximately 250 million dollars were invested on ceramic-matrix-composites (CMC) in the last decade (Ho92). The rapid advances in high modulus composite materials have been made possible by the recent emergence of new and improved reinforcing fibers (Gal89). These fibers can be combined with almost all materials (metals, plastics or ceramics) in various configurations to obtain properties superior to those attainable with either component alone.

Despite the scientific interest, technological importance, economical significance and continuous effort, no comprehensive understanding of high performance fiber reinforced ceramic composites has been accomplished (Maz90). Another study found that there are several areas which have technological research and development gaps (Mec89). These gaps resulted from a lack of uniform property measurements at high temperatures; a lack of a unified theory of interfacial bonding; a lack of knowledge of failure mechanisms for CMC's; and a lack of combined efforts from governmental, industrial and university research.

Fundamental studies of engineering ceramic composites are approached in several ways: theory and modelling to relate microstructural aspects to atomic units; chemistry for the synthesis of novel materials for fibers and matrices; processing and testing

procedures (Maz90). Table 2.1 summarizes potential application of CMC materials for the present and the future.

The goal of CMC research is to develop lighter, stronger, and more corrosion resistant materials capable of performing at extremely high temperature for prolonged periods of time. Currently CMC's exhibit increased fracture toughness and hardness, oxidation resistance and improved thermal shock resistance as compared with most monolithic ceramics. CMC's will be an emerging structural material of the next century by achieving cost-effectiveness, low density, high strength and toughness, and a low coefficient of thermal expansion.

At this point, no CMC materials have been manufactured that can be used at 1300°C or higher. The limitation of CMC's at elevated temperatures is attributed to the unavailability of high temperature fibers, high cost of processing or manufacturing methods, and lack of a design basis, methodology and life prediction tools (Gal89).

In the last decade (1979-89), CMC studies in the United States have made great progress. But the achievement by those research efforts was not enough to have adequate knowledge to design or predict the life of CMC components. There were factors of primary importance which were poorly addressed such as environmental factors, thermomechanical fatigue, erosion-wear-corrosion, multiaxial stress state and so forth

Current major applications of CMC's are cutting tool inserts, wear parts, space shuttle tiles and armor. They have been used to a very limited extent for engine component or hypersonic radomes in aerospace and military applications. Besides engineering technological factors, there were other factors to keep CMC materials

Table 2.1 Potential Markets for Ceramic Composite Materials (Ho92)

AREA	USES
Aerospace	bearings, combustors, fuel cells, fuel systems and valves, high temp. aux. power units, starters, seals, structures, thermal protection systems, turbine engine components
Automotive	catalytic converters, drive-train components, fixed boundary recuperators, fuel injector components, low heat rejection diesels, turbines, turbocharger rotors, valves and valve seats, water pump seals
Chemical Process	catalysts and igniters, mechanical seals, nozzles, radiant tubes and burners, recuperators, reformers, refractories, valve components
Bioceramics	artificial teeth, bones and joints, heart valves
Defense	armor, bearings, engine combustors, high performance radome materials, low observables, rocket nozzles, submarine shaft seals, tank power trains, ground support vehicles, helicopter and jet components
Electric Power Generation	bearings, ceramic gas turbines, cogeneration, filters(gas clean-up), fuel cells(solid oxide), high temperature components

Table 2.1 .. continued

AREA	USES
Electronics	advanced multilayer integrated packages, multilayer capacitors, pressure and gas sensors, substrates
Environmental	advanced components and systems for environmentally harsh processes, filter and scrubbers, incinerator liners and after-burners, radiant burners and boilers, waste water treatment
Industrial	boats, burners, crucibles and ladles, cutting tools and dies, insulation, molten metal filters, seeded gel abrasive for metal/ceramic finishing, heat exchangers, submersibles, HT tooling
Oil Industry	bearings, blast sleeves, flow control valves, pumps, refinery heaters

excluded from important applications: 1)health hazard during processing, manufacturing or handling; 2)high cost of fibers and whiskers; 3)lack of cost-effective manufacturing capabilities; and 4)lack of application data.

In the United States, there are many organizations and federal government offices that are concerned with the study of CMC materials. Additionally, there are many research programs studying CMC's (Ho92, She92). Among those, summarized in Table 2.2 are five principal programs. Besides the USA, there are several countries which have invested in CMC research. France, Japan, Germany, United Kingdom and Sweden are the most active five countries. About 150 million dollars was spent for the study of CMC materials during the last decade (Ho92).

The most important research and development directions in CMC are (Ho92)

1. reinforcement materials: development of strong and stable high temperature fibers and fiber coatings.
2. interface structure: chemical synthesis, reaction, microstructure, mechanical properties relationship between microchemistry and microstructure.
3. processing: cost-effective processing methods such as chemical vapor infiltration.
4. testing methodology: non-destructive testing and characterization.
5. design and analysis.
6. environmental durability: erosion, wear and corrosion.

Table 2.2 USA Research Programs for Ceramic Composite Materials (Ho92, She92)

PROGRAM	GOAL
CFPC (ceramic fiber precompetitive consortia)	to develop ceramic fibers for 1400 to 1650°C composites
CBTP (ceramic bearing technology program)	to enhance the industrial technology base capability for ceramic-based bearings in advanced defence systems
IHPTET (integrated high performance turbine engine technology)	to meet the need for ceramic composites capable at 1650°C or higher
HCST (high speed civil transport)	to develop environmentally acceptable and economically viable (~\$0.10/mile fiber) by pinpointing combustor and nozzles as critical to the success
HITEMP (advanced high temperature materials program)	primarily to meet the need for a civil-transport-engine

Mechanical Behaviors of Ceramic Fibers

The polymer-derived ceramic fibers, known to exhibit flaw-dependent brittle failure, are well-described by Griffith's classical fracture principles (Gri20). In other words, the strength of those fibers is determined by the size of largest flaw in them. An inverse relation between tensile strength and gage length is typical of brittle materials.

There are two well-known approaches to analyze the mechanical behaviors of brittle ceramic fibers: fracture mechanics/fractography and Weibull analysis. Figure 2.1 shows a schematic morphology of a typical fracture cross-section of brittle materials. The fracture initiates at the boundary of a flaw and slowly propagates to form a mirror region. Then it creates a mist region with a moderately increased crack propagation rate. A hackle region is produced when the crack propagation was accelerated to lead to an extensive crack branching and finally to a catastrophic failure (Say85).

The loci of brittle fiber fractures are found either on the surface or in the middle of fiber cross-sections. The former results from surface damage while the latter originates from particulate flaws included in the fibers. Surface damage occurs when fiber surfaces are handled poorly during the processing. Particulate flaws are mostly caused by gelled polymer particles or other external impurities (Maz90).

The usefulness of fracture mechanics/fractography for fiber studies depends on the fact that the morphology of a fracture surface is correlated to the properties of materials. A quantitative analysis of fracture surfaces would give valuable information about the cause and the progress path of material fractures. A feedback of fracture analysis results, to the materials and the processing, would bring an improvement of

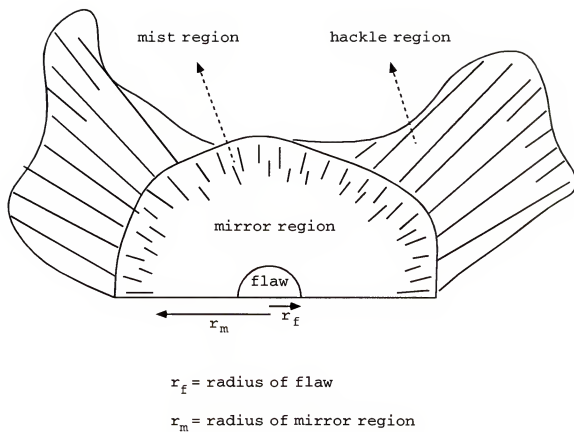


Figure 2.1 Schematic Morphology of a Typical Fracture Cross-section of Brittle Materials

material properties.

A quantitative correlation of fracture parameters to fracture stress was first formulated by Griffith (Gri20). Modifications have been made to the original Griffith equation (Eva74, Mec74). The first semi-empirical expression was formulated between flaw radius and fracture stress. The flaw size, however, is sometimes extremely difficult to measure precisely. Based on an assumption that the flaw size is linearly proportional to the mirror radius, the equation is given

$$\sigma_f r_m^{\frac{1}{2}} = B$$

where σ_f = fracture stress, r_m = mirror radius, and B = constant. From the Griffith-Orowan-Irwin equation (Her89), the relation between flaw radius (r_f) and material properties is

$$\sigma_f r_f^{\frac{1}{2}} = Y (2E \gamma_c)^{\frac{1}{2}}$$

where E is elastic modulus, Y is a geometric parameter and γ_c is fracture energy. Since the critical stress intensity (K_{IC}) is related to the properties by

$$K_{IC} = (2E \gamma_c)^{\frac{1}{2}}$$

the relation between flaw radius and material properties is given

$$K_{IC} = Y \sigma_f r_f^{\frac{1}{2}}$$

There are two main factors for a spread of experimental data: inherent inaccuracy in the test method and genuine variation sample-to-sample in properties. The measured property variation is extremely large ($\sim 25\%$) in a typical test of a small ceramic batch, compared to few percent in that of most metals. Weibull statistics is based on empirical reasoning although there is a small but increasing amount of theoretical justification for its use (Wei51).

$$P_S(V_0) = \exp \left[- \left(\frac{\sigma}{\sigma_0} \right)^m \right] .$$

$$P_S(V) = [P_S(V_0)]^{\frac{V}{V_0}}$$

where $P_S(V_0)$ is survival probability of volume V_0 , σ is tensile stress, σ_0 is normalization parameter, m is Weibull modulus and V_0 is unit volume. Typical m values are: ~ 5 for chalk, ~ 10 for engineering ceramics such as SiC and Si_3N_4 , ~ 100 for steel. A high value of m for a material means a high predictability of mechanical performance. Combining the last two equations, the Weibull equation is obtained:

$$P_S(V) = \exp \left[- \frac{V}{V_0} \left(\frac{\sigma}{\sigma_0} \right)^m \right]$$

Taking the natural logarithm twice on both sides,

$$\ln(\ln[\frac{1}{P_S(V)}]) = \ln(V) - m \ln(\sigma_0) + m \ln(\sigma)$$

If V is constant, as occurs in most cases, the Weibull modulus, m , can be calculated readily by a linear regression equation:

$$Y = a + mX, \text{ where } Y = \ln(\ln[\frac{1}{P_s(V)}])$$

$$a = \ln(V) - m \ln(\sigma_0)$$

$$X = \ln(\sigma)$$

$$m = \frac{\Sigma XY - n\bar{X}\bar{Y}}{\Sigma X^2 - n(\bar{X})^2}$$

If volumes of samples are not constant, but have a considerable variation, m can be calculated using a planar regression. For details, one can refer to a statistics textbook (Koh85).

There are a variety of algorithms to allocate $P_s(V)$ as a function of strength. The simplest one is as follows:

$$P_s(V) = 1 - \frac{i}{N + 1} \quad i = \text{strength rank}; 1, 2, \dots, N$$

Figure 2.2 illustrates a typical plot of $\ln\{\ln[P_s(V)]^{-1}\}$ versus $\ln[\sigma]$ whose slope, m , was measured as 3.86. The observation of a variation in Weibull modulus with respect to processing or heat-treatment of fibers would be an interesting subject to study. Weibull analysis of Nicalon SiC fibers was studied using a maximum likelihood method (Wu92).

Evolution of SiC Fibers

The performance or the value of engineering ceramic composite materials is determined to a great extent by the properties of the reinforcing ceramic fibers. Among the fiber materials, carbon fibers are an excellent candidate in a number of aspects such as high strength. However, due to an oxidation susceptibility, they may not be used for

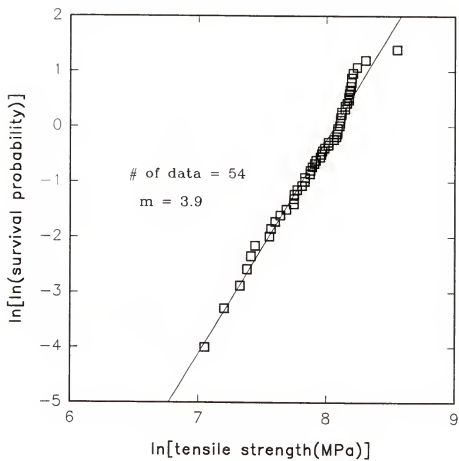


Figure 2.2 A Typical Weibull Plot: UF 127-12 SiC Fibers

composites in an oxidative atmosphere especially at elevated temperatures. Boron fibers are considered to have similar mechanical properties to carbon fibers.

After being produced with properties equivalent to those of boron fibers, SiC fibers have been considered to be very valuable for high temperature applications (Gal89). SiC/SiC composites are considered to meet most of the requirements for engineering ceramics because of these advantages (Yaj85): high tensile strength (up to 4.5 GPa), high elastic modulus (up to 485 GPa), excellent thermal shock resistance, good thermal and chemical degradation resistance, low thermal expansion, and high thermal conductivity.

Old forms of SiC fibers were fabricated by coating SiC via a chemical vapor deposition (CVD) technology on tungsten wires or carbon fibers. In the 1960s, General Technology started investigations to develop a process for preparing SiC fibers (Wit86). The SiC deposition on tungsten wire ($\sim 13 \mu\text{m}$) by a CVD process was performed at 1500°C . A number of gases were examined for carbon and silicon sources: $\text{SiCl}_4 + \text{C}_7\text{H}_8$, $\text{SiCl}_4 + \text{C}_3\text{H}_2$, $\text{SiCl}_4 + \text{CH}_3\text{I}$, $\text{SiBr}_4 + \text{C}_2\text{H}_2$, $\text{Si}_4\text{I} + \text{C}_2\text{H}_6$, $\text{HSiCl}_3 + \text{CO}$, CH_3SiCl_3 , $\text{C}_2\text{H}_5\text{SiCl}_3$, $(\text{CH})_4\text{Si}$ and $\text{Cl}_2\text{CH}_3\text{SiH}$. For many gases, hot spots occurred on the tungsten wires during deposition and the wires broke. Other wires such as titanium, nickel or molybdenum yielded a similar result.

Silicon carbide was deposited well with $\text{Cl}_2\text{CH}_3\text{SiH}$ at the lowest temperature. However, the best properties were attained by a deposition with CH_3SiCl_3 or $\text{C}_2\text{H}_5\text{SiCl}_3$ at 1100°C . $\text{C}_2\text{H}_5\text{SiCl}_3$ gas was more widely used due to a better availability. SiC fibers of 470 GPa modulus and of 100 micron diameter were produced. CH_3SiCl_3 was used

at the United Technologies Research Lab because it allowed a greater deposition rate. SiC fibers of 2.8 GPa tensile strength were manufactured. X-ray diffraction analysis of fibers showed that the deposited SiC was the β form (cubic) and the deposition was made preferentially for $\{111\}$ parallel to the fiber axis (Gal66).

Adding a boron deposition to the CVD SiC fibers resulted in a higher strength by keeping the grains small (Elk66). The effect of the boron content on the strength of SiC fibers was studied and it was found that the optimum Si:B ratio was about 6. SiC fibers of strength as high as 3.5 GPa and of modulus up to 449 GPa were obtained. The strength of SiC fibers tested at 1650°C was approximately one-fifth of that tested at room temperature.

Under a Navy contract, Tyco had attempted to replace tungsten wire with fused silica fiber. Glass fibers were coated with carbon followed by a SiC CVD processing. SiC fibers of 1.4 GPa strength and 414 GPa modulus were prepared. Due to a multiple coating, this approach suffered from a lack of uniformity in fiber properties.

Carbon substrate was studied by Avco, currently Textron (DiC80). Carbon filaments of 30 micron diameter prepared by a pyrolytic process were coated with graphite to enhance interfacial bonding. Coated fibers were processed via a conventional CVD process for SiC deposition. SiC fibers of 4.0 GPa strength and 400 GPa modulus were produced. Effect of a heat-treatment of SiC/W and SiC/C fibers on the fiber strength was studied (Ahm75). The tensile strength dropped significantly after the treatment at 1200°C or higher.

The emerging, and nowadays most widely used, route for producing continuous SiC fibers is through a preceramic polymer technology. Fabrication of economical continuous SiC fibers was possible after Yajima et al. (Yaj75) invented a method to process SiC fibers from a polymer precursor, polycarbosilane (PCS). A successful commercialization of Yajima's invention for Nicalon[®] fibers ignited a great deal of effort for other commercial polymer-derived SiC fibers such as Tyranno[®] (Si-Ti-C-O), HPZ[®] (Si-N-O-C) and others.

Silicon carbide whiskers are synthesized with reactant gases of SiCl₄, CCl₄ and H₂ in a vapor phase reaction equipment (Yaj85). Even though the diameter is not uniform and the production is costly, SiC whiskers are of high purity and high strength. According to a study (Lan89), SiC whiskers (single crystal; 0.3 to 1.0 μm diameter) exhibited tensile strength of 8 GPa and elastic modulus of 580 GPa.

Nicalon and UF SiC Fibers

The first polymer-derived SiC fibers were prepared by Yajima and his colleagues (Yaj75). PCS, polymer precursor for SiC, was synthesized and processed to produce SiC fibers. The PCS fibers were converted to SiC-based fibers by pyrolysis at presumably 1200°C. The PCS-derived SiC fibers were successfully commercialized by Nippon Carbon Company in Japan for *Nicalon*[®] fibers.

Even though they have been used predominantly for the reinforcement materials of CMC's, Nicalon fibers are restricted to use below 1200°C. This is mainly due to a significant decrease of fiber strength via thermal degradation at this point. The main

cause for the degradation has been known to be a high level of oxygen (~ 10 w/o) and the free carbon aggregates in Nicalon fibers. The oxygen is introduced into Nicalon fibers during a crosslinking process of spun polymer fibers. The crosslinking process is indispensable for the Nicalon fiber process to prevent green fibers from melting during pyrolysis.

The research of SiC fibers at the University of Florida was initiated in 1989, funded by the Defense Advanced Research Project Agency (DARPA) toward a development of SiC fibers with high temperature capability up to 1400°C. In the initial stage of the research, PCS was used for coating on ceramic materials. It was found that an increase in the molecular weight of PCS significantly reduced the melting tendency of PCS powders at 200 to 300°C. PCS of a molecular-weight greater than 9000 did not melt at all during the 1000°C pyrolysis. However, a high molecular-weight PCS was very difficult to process. It was also found that a small amount of vinyl polysilazane (10 to 15 w/o) incorporated with the high molecular-weight PCS worked very well not only to improve a fiber processability but also to enhance the chemical crosslinking via a hydrosilylation reaction.

According to a scanning Auger microscopy (SAM) analysis of fiber cross-sectional surfaces and a neutron activation analysis of ground fibers, UF SiC fibers contained an extremely low level of oxygen (~ 1 w/o). As a consequence, UF SiC fibers give much better tensile properties at elevated temperatures ($> 1300^\circ\text{C}$) than Nicalon fibers. Figure 2.3 illustrates a tensile strength retention curve of a UF fiber batch, compared to ceramic grade Nicalon fibers (Tore92). The research on SiC fibers at UF

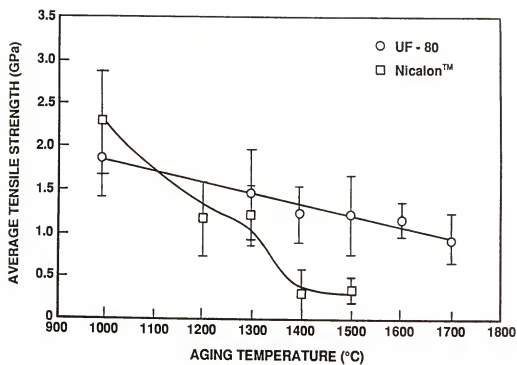


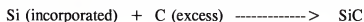
Figure 2.3 Tensile Strength of UF and Nicalon SiC Fibers:
Effect of Heat-treatment

continued to produce an excellent fiber batch, whose averaged tensile strength was above 3.5 GPa and with thermomechanical stability up to 1600°C. Degradation mechanisms of UF fibers as well as Nicalon fibers are being extensively studied.

Although a success has been attained from the fiber research at UF, there are some weak points. First, because the fiber processing at UF was all batch-type, reproducibility was not high and property variation from sample to sample, such as fiber diameter, was rather high, although averaged tensile properties of UF fibers are better than those of commercial SiC fibers. A scale-up work for a pilot plant is under way. Second, UF fibers showed a poorer stoichiometry between Si and C than Nicalon fibers. It means that UF fibers have more excess carbon content ($\sim 75\%$) than Nicalon fibers ($\sim 20\%$), which would explain why UF fibers have a low as-pyrolyzed elastic modulus. Third, there was virtually no study on CMC's using UF SiC fibers. The performance of SiC fibers in actual composites is so important that some research of composites containing UF SiC fibers is clearly needed.

According to XRD and TEM analysis, as-pyrolyzed UF SiC fibers were all amorphous in microstructure, while Nicalon fibers of a ceramic grade included crystalline phases to some extent. The low crystallinity of UF SiC fibers would result from low pyrolysis temperature (1000°C compared to presumably 1200°C for Nicalon fibers, based on their crystallinity), thermodynamically restricted crystallization by high molecular weight chains, branched chain structure, plasticizing action of short polysilazane chains, or insufficient number of nucleation sites during solvent drying/solidification.

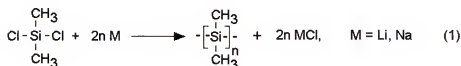
Several separate studies are in progress to enhance the fiber properties, especially tensile strength and elastic modulus at elevated temperatures, based on an improved stoichiometry. The main approach described here has been to incorporate excess silicon into the fibers to promote carbothermal reaction and to reduce the excess carbon level:

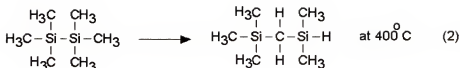


Polymer Precursors for SiC Materials

Synthesis of proper polymers is one of the most critical parts for polymer-derived ceramic fibers. Important features in the polymer synthesis are rheology (or spinnability), pyrolysis behavior, density and ceramic yield, and selectivity to the desired microstructure. Synthetic routes to SiC preceramic polymers could be divided into five categories (Lai92): 1)dehalocoupling of chlorosilanes to produce silanes or polysilanes, then convert them to PCS, 2)ring opening polymerization of cyclic silanes, 3)hydrosilylation to synthesize PCS, 4)dehydrocoupling to synthesize polysilanes, and, finally, 5)displacement and redistribution reactions of chlorosilanes. The dehalocoupling route has been studied most extensively.

The synthesis routes of PCS are totally based on two well-known chemical reactions: Wurtz dehalocoupling of chlorosilane, reaction (1) and Kumada rearrangement (Shi78, Sak66), reaction (2).





The earliest PCS (Yaj75) was made by the reaction (1) with chlorosilane and lithium catalyst to make dodecamethylcyclohexasilane, $-(\text{CH}_3)_2\text{-Si}]_6-$, which later was converted, via reaction (2), to PCS whose structure was supposedly, $[-\text{CH}_3\text{HSi-CH}_2-]_n-$. When molten sodium was used instead of lithium, polydimethylsilane (PDMS) was obtained by the reaction (1) (Yaj76). Then the PDMS was heated to 320°C in argon, melted, refluxed for 5 hours and then heated to 470°C to convert to PCS. This route has been used most commonly for PCS synthesis. Since then, there have been a number of studies for the conversion process of PDMS to PCS.

Pioneering studies on Nicalon-type SiC fibers and PCS were published in a series of articles (Yaj78, Has80, Has83, Has86, Ich86, Has88). Polydimethylsilane (PDMS) was synthesized from dimethyldichloro-silane in xylene with sodium catalyst (Yaj78). PDMS was converted to PCS in an autoclave by thermolysis reaction at 450 to 470°C for 14 hours. PCS has a structure similar to that of polysilapropylene (Yaj78). The pyrolytic conversion process of PCS to SiC fibers was studied using various chemical analyses (Has80). The conversion process was divided into three stages:

- 1st stage: condensation of polymers
- 2nd stage: thermal decomposition of side chains ($-\text{H}$, $-\text{CH}_3$)
- 3rd stage: crystallization of SiC

Using XRD and FT-IR, the conversion process was divided in six temperature ranges (Has83):

- 1st stage (100 - 350°C): evaporation of low m.w. components
- 2nd stage (350 - 550°C): dehydrogenation, dehydrocarbonation
- 3rd stage (550 - 850°C): decomposition of side chains
- 4th stage (850 - 1050°C): transition toward 5th stage
- 5th stage (1050 - 1300°C): SiC crystallization with dehydrogenation
- 6th stage (1300 - 1600°C): crystal growth

The structure of PCS was studied in more detail via intrinsic viscosity, NMR, and IR (Has86). The molecular shape of PCS was estimated to be planar and composed of rings. Figure 2.4 illustrates a schematic structure of branched PCS.

There were studies of the conversion mechanism and the composition-microstructure-property relationships extensively on the pyrolysis of Yajima' route PCS up to 1600°C (Bou91a, Bou91b). With various temperature profiles, gases and solid residues from pyrolysis of bulk or filaments were analyzed using TGA, extended x-ray absorption fine structure (EXAFS), gas chromatography-mass spectrometry, XPS, TEM, XRD, Raman Spectroscopy, Auger Spectroscopy, and electrical conductivity measurements. They concluded that a pyrolysis process is completed by four steps: (1) initial heating (20-550°C), where no remarkable chemical change is observed, (2) organo-metallic mineral transition (550-800°C), (3) nucleation of SiC (1000-1200°C), and (4) SiC grain coarsening (> 1400°C). Gases from the pyrolysis included CH₄, C₂H₆, CO, C₂H₄, and methylsilanes, whose contents were heavily dependent upon the pyrolysis

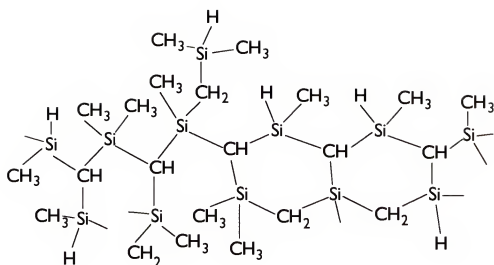


Figure 2.4 A Schematic Structure of Branched Polycarbosilane

temperature.

Polyborodiphenylsiloxane (PBDPSO) was used alternatively for the Lewis acid catalyst (Yaj77). A chemical analysis of PCS catalyzed by PBDPSO revealed that polymers have a significant oxygen content while the boron content was extremely low. A proposed role of PBDPSO (Yaj76) was to enhance the formation of silapropylene radicals, produced via the pyrolytic cleavage of Si-Si bonds. These reactions occur with formation of siloxane bridges and release of gaseous species containing boron.

The effect of adding PBDPSO as an accelerator on PDMS conversion to PCS was studied (Ich86). Addition of PBDPSO at concentrations of up to 5% to PDMS increased the yield of PCS. However, the resistance to oxidation was substantially reduced by the increased oxygen content in SiC fibers (Ich86). During pyrolysis, five elements were detected in PCS skeleton (Has88): silicon, carbon, hydrogen, oxygen, and boron. SiC fibers processed in different conditions were analyzed and empirical chemical formulae were obtained: $\text{SiC}_{1.77}\text{H}_{3.7}\text{O}_{0.04}$ for fibers derived from PC-470 and $\text{SiC}_{1.55}\text{H}_{0.03}\text{O}_{0.33}$ for Nicalon-type SiC fibers. If the main ingredients are SiC, SiO_2 , and free carbon, the contents of free carbon and SiO_2 are significantly higher in Nicalon-type SiC fibers.

Polydimethylsilane is known as an insoluble, infusible and therefore intractable polymer. A series of polysilane copolymers including phenyl moieties were studied (Wes83, Wes84, Wes86). Phenyl group incorporation was intended to enhance the solubility of copolymers in organic solvents. It was found that the phenylmethylsilane-DMS copolymers, or polysilastyrene (PSS) could be used for SiC polymer precursors. Copolymers of a molecular weight as high as 150,000 were synthesized. The resulting

random copolymers were soluble in most organic solvents, but hexane and alcohols.

It was found that polymethylsilanes (PMS) containing Si-H and/or Si-(CH=CH₂) moieties can be used directly for SiC precursors (Sch84, Sch86). Potassium or sodium was used for the preparation of PMS from chlorosilanes. The product was the polymer, (CH₃SiH)_X(CH₃Si)_{1-X} where X varied depending upon the reaction conditions. When X was greater than 0.65, the ceramic yield was pretty low, less than 20%. Sodium was used for dehalocoupling of CH₃HSiCl₂ to prepare PMS (Sey87, Sey89). Polymers were modified by hydrosilylation with organic or organosilicon compounds such as divinylbenzene and polybutadiene to increase the ceramic yield (60 to 70%).

Ceramic yield was correlated to the chain structure of polymer precursors (Cad90). They measured the chemical changes accompanying the pyrolysis via NMR, IR, and TGA. Polymers used were polysilane with various side groups. These were used instead of the polycarbosilane. Specimens were prepared by coating precursors on silicon wafers followed by pyrolysis. The phenyl side group with a small amount of vinylic silane gave the highest yield (even higher than theoretical value). Nevertheless, polysilane terpolymer offered a combination of high yield and easy processing. The chemical changes in polymethylsilanes (PMS) during pyrolysis up to 1300°C was studied using TGA, ²⁹Si NMR, and DRIFTS (Zha91). They visualized the pyrolysis process as

- a. PMS -----> PCS (at ~ 400°C)
- b. PCS -----> hydrogenated SiC (at ~ 600°C)
- c. SiC -----> β-SiC (at ~ 1000°C)

The formation of crystalline SiC was detected by sharp peaks, at 15.7 and 20.5 ppm, in NMR spectra. Since carbon could inhibit the grain growth, they mentioned that an optimum stoichiometry would be about $\text{Si}_{1.0}\text{C}_{1.1}$, which may be obtained by the pyrolysis of PMS copolymer with small amounts of aromatic silane.

Near-stoichiometric SiC was prepared from PMS with catalysts in a recent study (Sey92). Without a catalyst, $[-(\text{CH}_3\text{SiH})_{0.4}-(\text{CH}_3\text{Si})_{0.6}]_n$ gave a silicon-rich pyrolysis product with 60% ceramic yield: 75% SiC and 25% Si. With catalysts (zirconium cyclopentadienyl complex), a much less Si-rich product was obtained. The best case occurred with $[(\eta\text{-C}_5\text{H}_5)_2\text{ZrH}_2]_n$ catalyst when the pyrolysis of PMS at 950°C gave a solid product of the following composition: 98.0% SiC, 1.6% ZrC and 0.4% Si. This result may have a great potential to use with PCS which gives carbon-rich ceramic fibers. However, spinning these compositions may not be as straightforward.

Metal catalysts such as $\text{Ru}_3(\text{CO})_{12}$ increased the ceramic yield of PMS with photochemical irradiation (Lai90). The same treatment to the Nicalon PCS increased the ceramic yield as well. Pyrolysis of all PMS is known to give excess silicon while that of Nicalon PCS gives excess carbon. It was found that an appropriate mixture of those two polymers with $\text{Ru}_3(\text{CO})_{12}$ catalyst made a ceramic product of 99% SiC and 1% carbon. However, no further processing studies were reported.

Vinylc polymethylsilanes (VPS) were prepared by dehalocoupling $(\text{CH}_3)_x\text{SiCl}_{4-x}$ and $\text{CH}_3(\text{CH}_2=\text{CH})\text{SiCl}_2$ (Sch88, Schi83). Properties of resulting polymers were changed by the compositions. Copolymers and terpolymers were prepared using $\text{CH}_3\text{HSiCl}_2$, $(\text{CH}_3)_x\text{SiCl}_{4-x}$ and $\text{CH}_3(\text{CH}_2=\text{CH})\text{SiCl}_2$. The overall ceramic yield was low

ranging 17 to 44% depending on the composition. Other PMS polymers were polysilahydrocarbons prepared by coupling chlorosilanes to alkene such as styrene or isoprene (Sch86, Schi84). Even though a high ceramic yield was attained with $\text{CH}_3\text{HSiCl}_2$, it was less than 50%.

Characterization of SiC Materials

The overall characterization of ceramic materials has been classified into three categories (Han87): chemical, physical and mechanical analyses. In some occasions, boundaries between those categories may not be clear. Environmental analysis could be added to the classification.

Chemical analysis is carried out for chemical information either on the surface or in the bulk of materials. The surface characteristics of a thin surface layer may not be very important to the bulk properties of fibers such as tensile strength or density. However, there is a general consensus that interfaces in fiber-reinforced ceramic composite materials are very critical to determine overall mechanical properties (Cao90, Pre89). The interfacial bonding or slipping/failure is totally dependent upon the physical and chemical interactions between the fiber surface phase and the matrix phase.

For ceramic fibers, the bulk chemistry could be measured with powdered specimens. Spectroscopic methods such as x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and Fourier transform-infrared (FT-IR) have been used very frequently in surface chemical analysis. Several techniques for microanalysis were reviewed (She89). Bulk chemical compositions of several SiC (Kar91) and Si_3N_4

(Hom90) whiskers have been measured by the help of fusion analysis service companies. It was realized that the bulk compositions is very close to their stoichiometric proportions and that the oxygen bulk content in both whiskers are not very high (0.15 to 0.92 w/o).

X-ray photoelectron spectroscopy has been most widely used for quantitative chemical composition as well as chemical oxidation state identification. Thin films of SiO_2 and Si_3N_4 (Lic83, Laf89) on silicon, and single crystal silicon wafer (Miy82) have been characterized via an XPS. Surface chemistry of Nicalon SiC fibers (Laf89, Cla87) and other commercialized SiC fibers, powdered or not (Kar91, Hom90, Tay89), have been studied via XPS. Mg $K\alpha$, Al $K\alpha$ and Zr $K\alpha$ lines were used as x-ray sources. Calibration of binding energy of each photopeak could be based on Au $4f_{7/2}$ peak (at 83.8 eV) or hydrocarbon peak (CH_2 : at 284.6 eV). For electrically insulating specimens such as SiC and Si_3N_4 , the charging effect on the shift of binding energy must be considered.

A number of XPS results have revealed a significant level of inconsistency in binding energy values for carbon, silicon, and oxygen elements. This result could be caused by the neglect of charging effects. Taylor (Tay89) has shown that the oxygen Auger parameter and O 1s - Si 2p peak position difference could be used consistently irrespective of the extent of charging in various SiC powders and whiskers.

It has been shown that oxygen content (derived from SiO_2 , Si-O-C, and/or oxynitrides) of SiC fibers is much higher on the surface, ranging from 11.3 to 51.4 w/o, than in bulk. This is a good evidence of heavy oxidation on the outer surface of SiC fibers. A study of Si_3N_4 whiskers (Hom90) via XPS has shown a following typical surface composition: Si = 44.0 w/o, O = 14.4 w/o, Y = 12.9 w/o, C = 3.2 w/o.

Angle-resolved XPS could be a very useful technique to measure the chemical depth profile and film thickness. A thin film of SiO_2 caused by fortuitous oxidation on Si_3N_4 turned out to be about 0.6 nm via XPS (Lic83).

One of disadvantages in XPS is low spatial resolution. This is partly due to the rather low efficiency of photoelectron emission process. This means that XPS measurement of a filament of ceramic fiber (0.5 to 50 μm diameter) will require a device to focus the x-ray beam into a very small area. XPS measurement with a small sampling spot will take very long time. Hence, a bundle of fibers is usually measured together with a larger x-ray beam.

Auger electron spectroscopy (AES) and Secondary Ion Mass Spectrometry (SIMS) could be used as a complementary analysis to XPS. They have very good spatial resolution capability (submicron level). AES has been used in the studies of SiC single crystals (Miy82), $\text{SiO}_2/\text{Si}_3\text{N}_4$ thin film (Oos82) and SiC Nicalon fibers (Buns86). One thing to be noted is that even though XPS and AES all are known to be very surface-sensitive, there could be a considerable difference in their actual measurement depths. A remarkable discrepancy was observed between XPS and AES results on a SiC single crystal (Miy82). They pointed out that it was caused by the deeper measurement of XPS (~ 2 nm) than that of AES (~ 1 nm). AES Si LVV spectrum was reported to give a greater binding energy difference between oxide and nitride than Si KLL or XPS Si 2p (Oos82). However, the Auger Si LVV spectrum appeared a little broader.

If a simple chemistry, such as including two or three elements, is involved on the surface of a material, SIMS could have a great potential for chemical analysis. SiC and

Si_3N_4 fibers would be good cases; however, no extensive studies have been reported.

Fourier Transform Infrared Spectroscopy (FT-IR) has been one of the most popular analysis techniques in organic chemistry with various sampling techniques. SiC powders have been analyzed via diffuse reflectance (Tsu86), via photoacoustic (Tsu88) and via transmission (Ram89). It was observed that the photoacoustic technique offers easiest specimen preparation as well as high accuracy (Tsu88). Raman Spectroscopy was used and showed that SiC had a strong absorption at 785 cm^{-1} (Lag86).

Rutherford Backscattering Spectrometry (RBS) is known to be useful in characterizing thin films not only for chemistry but also depth profile (Gra89). A LPCVD Si_3N_4 on silicon was analyzed via RBS to measure the thickness of thin film (Tam82). An accurate density of thin film must be provided for a precise estimation, though.

X-ray Diffraction (XRD) has been employed to measure the existence of crystallinity in Nicalon fibers and the size of crystallites (Buns86, Jas89, Cla85). The width of XRD peaks increases as the size of crystallites decreases (Cul78). From a path-difference equation for two extreme angles, Scherrer formula was obtained as follows:

$$t = \frac{0.9\lambda}{B\cos\theta_B}$$

where t = crystallite size, λ = wavelength of x-ray ($1.5406\text{ \AA}$ for Cu $K\alpha$), B =FWHM of the peak and θ_B = Bragg angle. It has been most widely used to estimate the grain or crystallite size of small crystals from the measured width of their diffraction peaks. Nicalon NLP 101 SiC fibers were reported as amorphous (Buns86) and also as

microcrystalline (Cha88). Changes in the grain size of Nicalon fibers at elevated temperatures were investigated via XRD (Jas89, Cla85). Lattice parameters of some commercialized Si_3N_4 whiskers were measured (Hom90). The Cu $K\alpha$ x-ray line was used in all reported XRD measurements.

Electron microprobe (EMP) has been used to obtain chemical mapping on cross-sectional areas of fractured Nicalon SiC fibers (McK88). A high level of oxygen was observed on the surface of both NLP 101 and NLM 102 fibers, probably due to a thin oxide layer. An EMP measurement of Avco SiC fibers at an elevated temperature showed that the viscous melt phase observed at temperatures above 1350°C was silica (Buns86).

Solid-state nuclear magnetic resonance (NMR: ^{13}C and ^{29}Si) has been widely and powerfully used in SiC characterization. Cross-polarization and single-pulse magic angle spinning (MAS)-NMR, and surface-enhanced Raman spectroscopy (SERS) were used to characterize hot-pressed and sintered SiC bars (Dan90). Authors claimed they used MAS-NMR and SERS for the first time, in the characterization of SiC materials. It was also noted that SERS is very important for studies of polymorphism and inclusion of impurities (Dan90). Nine commercial SiC powders or bulk solids were characterized via ^{29}Si MAS-NMR (App91). Polymorphisms of cubic and hexagonal structures could be semi-quantitatively differentiated. Seven commercial β -SiC powders and one α -SiC powders were characterized using ^{29}Si MAS-NMR, TEM, and XRD (Car90). NMR was considered highly sensitive to the presence of stacking faults in β -SiC powders.

Another solid-state NMR study (Tai89) of PCS claimed that the conversion of precursors to SiC ceramics during the pyrolysis starts at 600°C and is completed at about 700°C. Pyrolysis of polytitano-carbosilanes was studied using ^{29}Si liquid MAS-NMR, TGA, IR, and XRD (Bab90). The precursor was obtained from PCS and titanium n-butoxide. The oxygen in alkoxide played an important role in forming the final products, Si-Ti-C. The maximum mechanical properties of Si-Ti-C fibers were obtained at around 1400°C due to the retention of amorphous phases at high temperatures.

Physical tests include the measurements of density, porosity, fiber diameter (thickness for thin film), thermal expansion coefficient as well as topography (Han87). Identification of defects (voids, impurities, dislocation density, etc) in ceramic structures could be added in physical tests.

Two standard methods for density of high modulus fibers are described in ASTM D 3800-79 (AST85). The Archimedes method could be used with good precision given a good chemical balance (up to 0.1 mg). Otherwise, the sink-float technique could be used. The density of a mixed liquid, whose density is the same as that of fibers, is measured using a hydrometer or pycnometer. A micropycnometer was used in a study of Si_3N_4 fibers (Hom90).

There is no standard method to quantify the porosity in ceramic materials. Instead, a ratio of actual surface area of fibers to nominal surface area would be measured and compared on a relative basis. The actual surface area could be measured by BET method with N_2 gas adsorption. For instance, Hg porosimetry was employed to measure porosity of B_4C powders (Lig88).

Fiber diameter can be measured using optical microscopy. The thickness of thin ceramic films could be measured via one of several spectroscopic techniques or Scanning Electron Microscopy (SEM) on fractured specimens. The surface can be observed by SEM and TEM. Various forms of SiC specimens, such as fibers (Kar91, Jas89, Cla85), particulate (McK88) and flexure bars (Kim90), have been studied via the SEM technique. It was shown (Ben87) that TEM could be much better in seeing the crystallinity in several ceramic powders. Nicalon SiC fibers (Bun86, Cha89) and other SiC fibers (Cha89) were studied via TEM combined with Dark Field-Electron Diffraction (DF-ED) or High Resolution Electron Microscopy (HREM). The resolution of TEM with HREM (Cha89) turned out to be about 24 nm. It was observed via TEM that Nicalon standard grade NLP 101 fibers had a lower excess carbon content than Nicalon ceramic grade NLM 202 fibers.

There have been a number of procedures to measure the thermal expansion coefficient of ceramic fibers. However, none of them were recommended as a standard method because of poor reproducibility (Han87). Flaws existing in the ceramic fiber structure are known to be very critical in determining the mechanical properties (Lam86, Ric85). Therefore flaw type and size are extremely important factors. One good example to support this proposition is that Nicalon fibers with shorter length or smaller diameter have greater tensile strength. It would be because the probability of crack propagation becomes lower in fibers of smaller dimension.

Among the non-destructive testing methods, the ultrasonic technique has a good potential to find the existence of voids in the bulk of fibers. The ultrasonic method has

been broadly used in the area of adhesion science. SEM and TEM techniques are useful in defect detection. On the surface of a SiC whisker (TA3), two Iwanga types of defects (type a: parallel stacking fault, type b: perpendicular stacking fault) were observed via STEM (Kar91). Despite its great importance, however, defect study has not been carried out extensively.

The principal mechanical tests for reinforcement fibers include the measurement of longitudinal tensile strength, elastic modulus, and failure strain. Other properties of interest could be creep, fatigue, bending, compressive strength, and so forth. However, the latter are generally not only difficult to measure but also of less importance in quality control testing or specification (Eri87).

A standardized tensile testing method of high modulus fibers is described in ASTM D 3379-75 (AST88). Gage length of 2.54 cm (= 1 inch) has been selected in several studies (Cla87, Buns86, Oka89). It is well known that stress-strain characteristic curve could be considerably dependent on strain rate. However, ASTM D3379-75 does not specify a strain rate. Instead, it recommends a strain rate that will take about one minute for specimens to break. The elastic modulus could be calculated from the tensile strength value and failure strain value. There are also alternate methods for measuring modulus (Eri87).

Analysis of materials after a heat-treatment at a high temperature and in an oxidizing atmosphere is very important in research of ceramic reinforcement materials. It is because, for instance, aerospace application of ceramic composites will need a high stability above 1300°C. Environmental tests will include the measurements of chemical,

physical, and mechanical changes at high temperature as well as in highly oxidative circumstances.

Various studies on the oxidation and thermal degradation behavior of SiC materials at elevated temperatures have been carried out. The thermal stability of SiC at high temperatures is known to be mainly due to the formation of a passive SiO₂ layer. Some atmospheric conditions, however, could cause the active oxidation reaction:



Plots of active-to-passive transition (as oxygen partial pressure versus 1/T) were obtained with various total pressures using a high temperature DTA-TGA (Vau90). The transition temperature of sintered α -SiC materials for passive-to-active behavior ranged from a low of 1347°C to a high of 1543°C for partial pressures of oxygen of 2.5 and 123.2 Pa, respectively. The effect of oxidation conditions for sintered α -SiC flexure bars when heated up to 1400°C in argon (including oxygen as a control variable) was measured via the 4-point-bend flexure test (Kim90). Active oxidation resulted in significantly reduced flexural strength of SiC bars and the strength was strongly influenced by the oxygen pressure, as well as the exposure time. Luthra (Lut91) has calculated the parabolic rate constants for the oxidation of SiC powder. He concluded that the oxidation was influenced by both interfacial reactions and diffusion.

The high temperature behavior of Nicalon SiC fibers have been studied extensively (Cla87, Buns86, Cla85, Lut91, Kim91, Ben91, Wan91). Tensile strength of Nicalon SiC fibers was measured by heating up to 1400°C in H₂ or in air (Kim91). Two

atmospheres were considered: H_2 + water vapor, and air. The variables were water vapor partial pressure, exposure time and temperature. Tensile testing was carried out at room temperature after high temperature heat treatments. The degree of thermal degradation was strongly related to the structure of SiO_2 (whether active form or passive form). At temperatures greater than $1400^\circ C$, a bubble oxide formed, which is supposedly responsible for the crack initiation.

Changes in microstructure and in strength of Tyranno and Nicalon SiC fibers after two thermo-chemical treatments up to $1600^\circ C$ was measured in N_2 , $N_2 + C$, and CO (Zho91). The carbon packing in flowing N_2 resulted in higher strength at all temperatures up to $1600^\circ C$. The purpose of the heat treatment in CO atmosphere was to inhibit the active oxidation. It was suggested that high temperature thermo-chemical stability of SiC materials will be highly improved if the evolution of CO is restricted. Growth of SiO_2 on SiC whiskers (Tokai^R) was studied using XPS (Rub91). At temperatures of 600 to $800^\circ C$, the surface chemical reaction was the rate-determining step and the oxide thickness was linearly dependent upon the oxidation time. Zhou et al. (Zho91) observed phase transformations in carbothermally-derived SiC, from α to β , as being processed at temperatures from 1800 to $2000^\circ C$. Corrosion characteristics of Nicalon fibers in HNO_3 solution were measured using IR, SEM, and absorption of nitrogen or benzene (Dan90). The corrosion initiated from some active sites so that surface roughness was substantially increased.

Preparation of Si and SiC Particles

For a better homogeneity and/or a reduced reaction time, the size of particles being incorporated with preceramic polymers should be much smaller than about one micron. A few suppliers, such as Matheson and Cerac, are producing Si and SiC particles of about one micron averaged size, there is no supplier for submicron particles. Therefore, fine and pure particles should be produced in the lab. There have been a few studies of preparing Si and SiC particles in the lab. Key features for each method is summarized below.

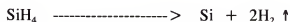
The first approach was to crush a bulk piece of silicon into fine particles. An arc-plasma method was introduced (Tan87). A bulk Si wafer was subject to a torch in a customized arc plasma furnace with tungsten inert gas (TIG) welding machine. The atmosphere was either argon, nitrogen or hydrogen. Two size groups of spherical particles were produced: 20-50 nm and about 10 μm . Another method is to utilize porous Si wafers. There have been a number of studies on the porous silicon ever since a photo-luminescence was obtained from an electrochemically etched, porous Si wafer surface. A fine Si particle solution in toluene was obtained by ultrasonication of the porous Si wafer in toluene (Hen92). The Si particles have an irregular shape and a fairly broad size distribution ranging from few nm to several μm . The actual particle size or the solid content was not reported. However, the content of nano-sized particles in the solution appeared very low.

In many cases, Si particles were prepared by various gaseous reactions activated by powerful energy sources. CO_2 -laser was used to produce Si particles from SiH_2Cl_2

in a stainless steel reactor (Bau90). The reactor is referred to as Laser Chemical Vapor Precipitation Reactor (L-CVP). The power of CO₂-laser was 150 W. Dark brown particles of amorphous Si were produced with a mean particle size of 50 nm. Small amounts of chlorine impurities were detected in the products. SiH₄ was decomposed to obtain Si particles (Kra88). Si particles were produced by heating silane gas with a CO₂ laser (130 W). The reaction zone temperature was set at 1400°C by adjusting the laser power input. Si particles formed at the intersection (of SiH₄ flow and laser beam) were carried by the carrier gas to a filter. Si particles of high purity (< 200 ppm total metals) and small size (40 - 2000 nm) were produced.

In another study, Si particles were obtained by reacting SiCl₄ with magnesium (Jon92). The reaction was conducted in a stainless steel reactor with an electrostatic precipitator (ESP) to collect the particles. The reaction temperature was measured as 950 to 1050°C and Si particles of submicron size were obtained. However, an actual size distribution or a particle shape was not reported.

Another possible method to prepared fine Si particles is through *sonochemistry*. It was suggested at UF as an idea, but yet to be studied (Bat92), to employ the chemical effects of ultrasound (*sonochemistry*). The silane gas is put into a toluene bath as very tiny bubbles. At an appropriate frequency of ultrasound in a well-designed container, silane bubbles can go through a decomposition reaction to form ultra-fine silicon particles in toluene:



The chemical effect of ultrasound is known to arise from the physical process of cavitation in a liquid (Sus89, Sus90). The liquid molecules are pushed together during the compression cycles of ultrasonication while they are pulled apart during the expansion cycles. The amount of negative pressure required to create cavities in the liquid depends upon the liquid itself. Pure water, for example, needs more than 1000 atmospheres of negative pressure. However, most liquids require much less pressure due to a sufficient contamination of tiny particles. The gas trapped on the tiny particles reduces the tensile strength of liquids so that much less pressure than 50 atmospheres is enough for the effect.

A bubble in a liquid is inherently unstable. Tiny bubbles will grow at the rate determined by the actual level of ultrasound frequency. A critical bubble size where the ultrasonic energy is absorbed most efficiently will be reached at some point. The critical size depends upon the wave frequency. Once a cavity experiences a very rapid growth, it can no longer absorb energy as efficient from the ultrasound wave. Without this energy input, the cavity can no longer sustain itself, the liquid rushes in and the cavity implodes. This implosion creates a local hot spot with a typical measured temperature of 5500°C. The temperature was estimated by monitoring some high temperature reactions. Another alternative method to create cavity implosion in a liquid is to use electrical microdischarge (Mar85). They are, however, found to be much less consistent than the ultrasound source (Fli89).

The methodology to produce fine SiC particles is almost the same as that for fine Si particles. Differences would relate to the reaction conditions as well as the reagents.

The first approach to introduce is to crush Si or SiC bulk into fine particles using an arc plasma. A Si wafer was torched in a plasma under an atmosphere of argon, CH₄ and H₂ (Ino89). The apparatus was exactly the same as that used in the arc-plasma preparation of Si particles (Tan87). The hydrogen played an important role in the conversion reaction. SiC particles compounded with polymorphism (2H, 4H, 6H and 15R for α -SiC, and 3C for β -SiC) were produced. The conditions with excess Si were inclined to produce β -SiC. It was proposed that CH₄ is dissociated in the arc plasma and dissolved in the molten Si bulk to form SiC. SiC sublimates to make ultra fine SiC particles.

A preparation of fine SiC particles from a SiC bulk (containing 10% Si) was studied (Nar90). A customized arc plasma furnace was used. Compared with bulk Si, no melting of bulk SiC occurred by the arc plasma irradiation. A pure argon atmosphere was most effective for the production of SiC particles. XRD analysis elucidated that bulk SiC of α -phase is converted to SiC particles of β -phase by arc-plasma processing. 20 to 100 nm size particles were obtained.

A study (Ish89) revealed that the synthesized particles are very dependent upon the gas moiety. Spraying of NH₃ in the arc plasma processing of Si bulk resulted in forming amorphous Si₃N₄ while the spraying of CH₄ formed SiC plus free carbon. This method looked useful because it can be applied to many other materials such as TiC, WC, AlN, etc.

SiC particles were obtained by reacting sand silica with carbon black (Krs92). The reaction was monitored at temperatures between 1450 and 1800°C. Compared with the well-known Acheson process, it was found the mechanism for the SiC formation

reaction is a function of the temperature. At temperatures below 1400°C, a solid state reaction between SiO₂ and C to make SiC was dominant. At temperatures well above 1400°C, the SiC formation was determined to a great extent by the availability of gaseous SiO. In all cases, almost pure β -SiC particles of 0.1 to 1.1 μm were obtained.

The SiH₄ reacted with C₂H₄ to produce SiC when activated by CO₂-laser (Suy85). The temperature at the center of the laser flame was measured as 1550 to 1750°C. β -SiC particles of 19 to 49 nm were obtained. By adding B₂H₆ gas in the sources, boron-doped SiC particles of about 100 nm were also obtained. SiC particles were obtained by another source, SiH₂Cl₂ (Suz92). The reaction flame temperature was 1000 to 2800°C. The composition of the reaction was controlled by the C₂H₄:SiH₂Cl₂ ratio. According to TEM analysis, the product was agglomerated SiC particles whose average size is about 0.2 μm .

SiCl₄ was used for the Si source gas in some studies. A gas phase reaction between SiCl₄ and CH₄ in d.c. thermal plasma produced β -SiC of narrow size distribution at 0.1 μm (Ala91). A commercial d.c. plasma arc was used. The particle size and the composition of the product was changed by the ratio of feed gases. A hybrid plasma reactor, combining d.c. arc jet and RF plasma, was used to react SiCl₄ with CH₄ (Egu93). SiC particles of a broad size distribution (5 to 200 nm) were produced.

Carbides and Silicides

Compared to other metallic compounds, such as nitrides, oxides, silicides or sulfides, carbide materials have a great potential for the refractory application. As

illustrated in Figure 2.5, carbides generally have higher melting temperatures than any other binary refractory materials (Vla64).

The usefulness of ceramic materials as a refractory or other high temperature applications is not solely determined by their melting temperatures. There are many other factors or properties to be taken into account prior to determining whether a material is suitable for the desired application. For an example, SiC has a lower melting temperature than many metallic carbide materials. However, the creep resistance of SiC at 1500°C is better than almost any carbide material of higher melting temperatures. Table 2.3 summarizes some properties or features of selected potential carbide materials. Even though the information was obtained through several sources, there is still lack of data so that a direct comparison may not be available in some occasions.

Many silicide materials are available for the carbide formation reactions with excess carbon found in polymer-derived SiC fibers. The most pronounced requirements for the candidate silicides materials would be: 1) low melting temperatures compared to its carbide, 2) good reactivity with excess carbon and possibly 3) availability in an ultra fine particle form. Table 2.4 summarizes selected silicide materials with melting temperatures and particle sizes of commercial products.

Densification Behavior of SiC

Silicon carbide is a principal candidate material for high temperature and high strength application in such areas as gas-turbine and turbocharger rotor components. The desirable properties of SiC materials result from the bonding characteristics, which is

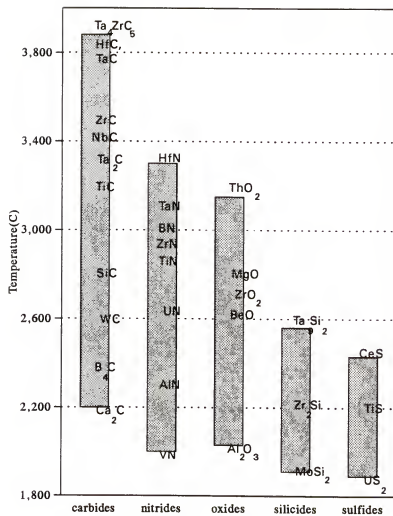


Figure 2.5 Melting Temperatures of Binary Refractory Materials

Table 2.3 Summarized Properties of Selected Carbide Materials

Property	SiC	B ₄ C	HfC	NbC	TaC	TiC	VC	ZrC
m.p.(°C)	2700	2450	3880	3430	3880	3150	2870	3530
density(g/cc)	3.21	2.52	12.20	7.69	13.96	4.59	15.65	6.90
severe oxid'n in air(°C)	1400-1700	1100-1400	1100-1400	1100-1400	1100-1400	> 1200	500-800	1100-1400
stability in helium	sublimes at 2350°C	stable to 2250°C	stable over 2230°C	stable to m.p.	stable to m.p.	useful to 3000°C	stable to 2400°C	useful to 2230°C
stability in hydrogen	attacked at 1350°C		stable to 2000°C	stable to 2200°C	useful to 2000°C	stable to 12-2200°C		stable to 2200°C
stability in oxygen		stable to 540°C	oxidize at 1370°C				burns in oxygen	oxidizes at 980°C
stability in nitrogen	stable		likely to nitride	stable to 2500°C	stable w/o hydrogen	reacts over 1500°C		nitrides at 1500°C

Table 2.3 .. continued

Property	SiC	B ₄ C	HfC	NbC	TaC	TiC	VC	ZrC
stability in H ₂ O			stable to red heat		burns at 800°C	stable to 650°C	stable to 800°C	stable at red heat
stability in other gases	reacts with CO ₂			decarburize sl. in air		reacts with CO ₂ (1200)	reacts w. Cl ₂	
max. use T in air(°C)	1100-1600	~1000						
weight change at high temp.	2%(3hr at 1400°C/air)	32%(3hr at 1400°C/air)				8%(3hr at 1400°C/air)		40%(3hr at 1400°C/air)
high temp. creep			slight at 2200°C	severe at 2190°C	severe at 2200°C			
RT strength (MOR)(GPa)	0.34(20°C)	0.34(RT)	0.24(RT)	0.25(RT)	0.21(RT)	0.23(RT)	0.07	0.16(RT)
HT strength (MOR)(GPa)	0.17(1300) 0.08(1400)	0.29(650) 0.24(1100)	0.09(2000) 0.03(2200)	0.02(2000)	0.12(2000)	0.09(2000)		0.06(1250) 0.02(2000)

Table 2.3 .. continued

Property	SiC	B ₄ C	HfC	NbC	TaC	TiC	VC	ZrC
tensile strength(GPa)		0.16(980)			~0.29	0.12(1000)		0.11(RT) 0.10(1200)
compression strength(GPa)	0.56	2.85(RT)				1.31	0.61	1.64
Young's modulus(GPa)	401(RT) 340(1400)	448(RT)	424(RT)	448(RT)	286-630 (RT)	439(RT) 379(1000)	270	317(RT)
shear modulus(GPa)	168(RT)	185(RT)						124(RT)
bulk modulus(GPa)	97(RT)	254(RT)						214(RT)
torsion modulus(GPa)			182(RT)		163(RT)			
poisson ratio	0.187	0.207	0.155		0.172	0.185		0.257
Mohs	9.2	9.32		9-10	9-10	9-10	> 9	8-9

Table 2.3 .. continued

Property	SiC	B ₄ C	HfC	NbC	TaC	TiC	VC	ZrC
Vickers h. (kg/mm ²)	3000-3500 (25g)	2400-3700	2530-3200 (50g)	2400(50g)	1800(50g)	2900-3200 (50g)	2800 (50g)	2600 (50g)
Knoop h. (kg/mm ²)	2500-2550 (100g)	2800-3100 (100g)	1790-1870	~2000 (100g)	1800-1950 (50g)	1900-2470 (100g)	2080 (100g)	2138
resistivity (ohm-cm)	10 ³ -10 ⁵	0.3-0.8	4x10 ⁻⁵ (4K) 6x10 ⁻⁵ (RT)	0.7-1.5 x10 ⁻⁴ (RT)	3x10 ⁻⁵	7-9x10 ⁻⁵	1.6x10 ⁻⁴	6.4x10 ⁻⁵ (RT)
structure	hexagon(α) cubic(β)	rhombic	fcc	fcc	fcc	fcc	fcc	fcc
thermal(cgs) conductivity	0.1(RT) .006(1250)	0.07(RT) 0.20(425)	0.053	0.034- 0.041	0.053	0.04(RT) .014(1000)		0.05(RT) 0.09(1200)
thermal expansion (10 ⁻⁶ /°C)	4.6(~500) 5.9(25- 2500°C)	4.5(~800) 7.1(25- 2500°C)	6.6(~612) 6.3(25- 1000°C)	6.9(RT) 7.5(25- 1500°C)	6.3(~600) 8.4(25- 2500°C)	6.5(~500) 7.9(25- 2500°C)		6.5(~500) 7.7(25- 2000°C)

Table 2.4 Properties of Purchased Silicide Materials

substance	melting point (°C)	particle size (purity %)	
		Aesar	Cerac
HfSi ₂	1680	325 mesh (99)	100 mesh (99.5)
NbSi ₂	1970	100 mesh (99.9)	325 mesh (99.5)
NiSi ₂	1120	80 mesh (99)	80 mesh (99)
Si	1410	325 mesh (99)	--
Ta ₅ Si ₃	2500	--	325 mesh (99.5)
TaSi ₂	2200	325 mesh (99.5)	325 mesh (99.5)
TiSi ₂	1760	325 mesh (99.5)	325 mesh (99.5)
Ti ₅ Si ₃	2130	325 mesh (99.5)	325 mesh (99.5)
ZrSi ₂	1700	--	325 mesh (99.5)

predominantly covalent with only 9 to 12% of ionic character.

It is well-known that substances with strong covalent bonding do not sinter easily. This is because that the covalent bonding is too strong (high bonding energy) to allow the enough vacancy diffusion for sintering (Pro75a). Due to the high grain boundary energy-to-surface energy ratio, pure SiC is not easy to densify. Directional bonding inhibits the vacancy diffusion, and instead promotes the surface diffusion which becomes dominant (Pro75a, Pro75b).

Sintering of pure SiC does not occur without high pressure or some additives. A densified SiC can be prepared in three ways (Omo82): reaction sintering, hot-pressing, and pressureless sintering. Densification of SiC by hot-pressing was pioneered by Alliegro (All56). Nowadays, however, it is not frequently used due to the low versatility. A compact of hollow SiC particle was reaction sintered for a thermoelectric energy application (Pai91). The sintering was attained at low temperatures (1200 to 1580°C).

Pressureless sintering, mostly, is carried out with additives. Sintering additives can be classified into two principal categories: liquid-forming additives (oxides) and solid-state sintering additives (nonoxides). There have been a variety of studies for both types of additives. The effectiveness of a sintering additive would be decided by several factors: sintered density (relative to the theoretical density), extent of grain growth, sintering temperature and time, characteristics of phase transformation, and so forth.

Many metal oxides have been used in SiC sintering. Generally, however, oxide additives are believed to give a limited density (up to 90%). Oxides such as MgO, Y₂O₃,

Al_2O_3 , and SiO_2 , are melting or forming eutectic during the densification at the sintering temperature.

Several metals and metal oxides were evaluated as additives, based on the free energy consideration of reaction (Neg86). It was noted that sintering aids should not decompose SiC during sintering. Among oxides, most widely used are Al_2O_3 and Y_2O_3 . 95% densified SiC was obtained by sintering at 1850 to 1950°C with Al_2O_3 and Y_2O_3 . Al_2O_3 was prepared as a product of reaction between $\text{Al}(\text{OH})_3$ and HCl , while a reaction between $\text{Y}(\text{OH})_3$ and HCOOH was used for Y_2O_3 (Omo82).

Silicon carbide was sintered at much lower temperature with Al_2O_3 if some free carbon was present (Mis91). Mechanisms for three cases were proposed: at first, with no excess carbon, molten aluminum reacts with SiC, secondly, SiC- Al_4C_3 eutectic is formed if free carbon is present. Finally if SiO_2 is present, mullite can be formed.

It was observed that the small amount of SiO_2 present combined with Al_2O_3 and Y_2O_3 on the SiC surface enhanced the sintering of SiC. The agreed advantages of oxide additives are: rapid sintering, limited grain growth (to 1.5 μm), suppressed transformation of β -SiC to α -SiC (Mul91).

Carbon and boron are most widely used as non-oxide sintering additives. 99% densification was attained with C and B for solid-state sintering of SiC. Prochazka pioneered the research in pressureless sintering of SiC (Pro75a, Pro75b). He has studied the densification behavior of SiC associated with C or B content. He has proposed that the lower limit content of B or C is related to the solubility of B or C in SiC so that the content of either element has to be greater than the solubility limit. He determined

optimal contents of C and B are 0.25 and 0.30 w/o, respectively.

Amorphous and crystalline boron, B_4C , $LiBH_4$, and H_3BO_3 were used for boron addition (Pro75a, Pro75b). The first three substances made good sintering additives, while H_3BO_3 did not give a good densification. This was attributed to the severe evaporation of B_2O_3 during sintering. Polymethylphenylene (PMP) and carbon black were added for carbon. PMP was effective enough to give a good densified SiC structure. He concluded that one of the key factors that enables the solid-state sintering of SiC with C and B to work well is the decreased grain boundary energy-to-surface energy ratio. Boron, by a preferential segregation, will decrease the grain boundary energy while carbon will increase the effective surface energy by removal of SiO_2 or free Si (Pro75a, Pro75b, Hau80).

It was observed (Han80) that at 2000 to 2100°C, β -SiC is very likely to transform to α -SiC. β -SiC (cubic) is a thermodynamically metastable state among the polymorphic SiC, while α -SiC (hexagonal) is a stable structure (Hei91). Electron donors, such as boron, were predicted to be favorable as additives for β -SiC sintering.

Another study (Hau80) found that B_4C and BP were the best additives for α -SiC sintering while boron worked the best for β -SiC sintering. Also, the effect of the atmosphere on the densification was studied. The best densification result was obtained with inert gas, whereas nitrogen was observed reducing the effectiveness of additives. Carbon monoxide caused some loss of boron to result in less densification. It was suggested that a smaller size particle and a higher surface area of SiC are better for the densification.

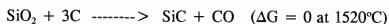
Various techniques, such as STEM, AES, wavelength dispersive x-ray analysis (WDXA), SIMS, microautoradiography, were used to characterize the boron-containing phases in sintered α -SiC. The α -SiC lattice was saturated with boron. An additional annealing at lower temperature caused the nucleation and grain growth of fine B-containing precipitate. In all cases, no boron (in any form) was detected on grain boundary (Mor86). In another study (Lan88), however, Si-containing B_4C was found throughout all α -SiC grains, which would interact with the extensive number of dislocations.

The change of lattice parameter during SiC sintering was measured (Taj82). The addition of boron as an additive decreased the lattice parameter. Several studies on the mechanism of boron diffusion, however, gave contradictory results: Some have suggested that the boron substitutes for silicon in SiC while the other have proposed that the boron substitutes for carbon in SiC. According to one experimental study (Taj82), the boron can substitute for silicon or the carbon about equally to form stable compounds like B_4C or SiB_4 . Similarly, there has been a huge disagreement on the relative diffusivity of silicon and carbon. According to some studies, the silicon diffuses faster than the carbon. But the reverse is true in other studies, where it was observed that boron enhances the overall chemical diffusivity (Fri83).

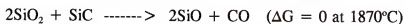
Carbon has been known to have two principal functions in SiC sintering (Ham89): to eliminate the thin layer of SiO_2 on SiC and to catalyze the densification. Addition of carbon is necessary in SiC sintering no matter what type of other additives are used (Ham89). If the dispersion of carbon is not homogeneous, however, the carbon may

form agglomerate type critical flaws so that its presence could be detrimental to the densification. The inclusion of carbon was examined on UHV exposed fracture surface via AES. The author insisted that the homogeneously dispersed carbon improved deoxidation of SiC powder, enhanced sintering efficiently, and reduced the number and the size of inclusions.

Literature data on self-diffusion of SiC were used to identify the functions of excess carbon in SiC sintering (Rij90). The excess carbon reduces SiO₂ by the reaction below:



The excess carbon also enhances the rate-controlling bulk self-diffusion rate of SiC by one hundred times. The formation of SiO could cause the vapor transport, which not only inhibits densification but also leads to coarsening. At a higher temperature,



Boron Precursors

There have been a number of studies on the precursors of boron ceramic materials. This is either to obtain pure boron compounds for main products, or to introduce boron compounds as additives. Precursors include preceramic oligomers, polymers and gases. As described earlier, boron incorporation to the polymer-derived SiC fibers is necessary to enhance the thermomechanical stability at elevated temperatures. This section summarizes some published studies on boron precursors,

other non-published candidate materials for boron addition and key features of decaborane, the substance studied here.

Polymer chemistry for boron precursors has been studied extensively at MIT. A few phosphorus-containing polymers were synthesized and pyrolyzed to obtain ceramics (Ree88). The highest ceramic yield was attained with $-\text{Ph}_2\text{POPPh}_2-$ in the polymers, whose pyrolysis products were composed of boron, carbon, oxygen and phosphorus. Decaborane was used as a starting material for the synthesis of polymers. The known structure of a typical polymer is $[-\text{B}_{10}\text{H}_{12}\cdot\text{Ph}_2\text{POPPh}_2-]_n$. According to chemical analysis results, the pyrolysis product has a large quantity of free carbon, residual oxygen and phosphorus (Sey89). Besides, a significant porosity was developed in a bulk body. It was suggested that a reactive excess boron is needed to consume the free carbon and enhance the stoichiometry.

Since the phosphorus-containing polymers made undesirable ceramic products, the effort was shifted to amine-containing polymers (Ree88, Ree89). The structure of a typical polymer was $[-\text{B}_{10}\text{H}_{12}\cdot\text{diamine-}]_n$. A variety of diamine moieties were incorporated: $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{NH}_2$, $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ and so forth. The highest yield (89%) was attained when $\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$ was used. A pyrolysis at 1000°C in argon produced a mixture of B_4C , BN and free carbon. The ratio between those compounds varied with the amine moiety incorporated in polymers. On the other hand, a pyrolysis in NH_3 resulted in mostly BN. The free carbon content was significantly reduced by the pyrolysis in NH_3 . Another polymer was studied: polyborasilazane (Sey90). It was prepared by reacting $\text{H}_3\text{B}\cdot\text{S}(\text{CH}_3)_2$ with $[\text{CH}_3\text{SiHNH}]_n$,

cyclic oligomers. A black borosilicon carbonitride was obtained when the polymer was pyrolyzed in argon while a white borosilicon nitride was produced when pyrolyzed in NH_3 .

Hexagonal-BN was produced when polyborazene (or polyborazinyl amine) was pyrolyzed at 1000°C (Rye90). It was found that gas evolution was complete at a temperature below 400°C . The same polymer was sprayed as aerosol droplets to produce fine powders (Lin91). The droplets were thermally decomposed at 1000°C to make amorphous BN. Liquid ammonia was used for solvent. Polymeric cyanoborane, $[-\text{CNBH}_2-]_n$, was used for a plasma enhanced chemical vapor deposition (PECVD) of BN coating (May90a). A severe contamination by paracyanogen was detected and the produced BN was boron-deficient. BN was obtained from the pyrolysis of two oligomeric polysilaborazines (Pac88).

A BN precursor was used for a binder of BN densification (May90b). The precursor was prepared by a partial condensation of 2,4,6-trichloroborazine and bis(trimethylsilyl)acetylene. Catalyzed by AlCl_3 , a pyrolysis at 800°C of the precursor resulted in a BN-rich residue, which was then mixed with BN powders for a hot pressing. A pressure pyrolysis of borazine (700°C at 100 MPa) gave amorphous BN with 60% ceramic yield (Hir89). The amorphous product was converted to cubic BN when it was heat-treated at 1200°C and under 6.5 GPa with a AlN catalyst.

Organic precursors have been added as sources of boron (Pas91). Carborane ($\text{B}_{10}\text{H}_{12}\text{C}_2$) and amino boranes have been used as precursors for B_4C on pyrolysis. Polyphenylbor ($[\text{C}_6\text{H}_5\text{B}]_n$) has been known as a precursor for boron and carbon.

Pyridine-borane ($\text{BH}_3 \cdot \text{C}_5\text{H}_5\text{N}$) was observed to give a suitable B:C ratio. A high homogeneity of boron and carbon was attained by the liquid-phase precipitation. High densification (99% at 2200°C), retarded grain growth, and equiaxed fine grain (about $1.3\ \mu\text{m}$) were accomplished.

Two factors are important in evaluating the candidate boron precursors: One is homogeneity. The importance of uniform distribution of boron precursors cannot be overemphasized. A second factor is pyrolysis efficiency. The boron precursor, upon pyrolysis, must be converted to a corresponding boron compound with a reasonable ceramic yield.

The precursor has to be uniformly mixed with polymer precursors for SiC fibers and they should be processed together without an appreciable phase separation. Therefore, our boron precursor must stay as a solid at 25 to 80°C . It has to be very soluble in toluene or other solvents along with PCS or PCS copolymers. Table 2.5 lists potential materials found among commercial products. Decaborane was the first substance selected for this study.

Decaborane(14) is one of the well known and commercially important boron hydrides. The molecular structure of $\text{B}_{10}\text{H}_{14}$ is shown in Figure 2.6. B_{10} -cage has an open, 6-atom face which exhibits a boat conformation. Four of the six edges of the face are asymmetrically bridged by hydrogen atoms ($\text{B}-\mu\text{H} = 1.298$ and $1.347\ \text{\AA}$) (Hou90). The unbridged B-B edges are significantly longer than the bridged B-B separations. Decaborane is a colorless crystalline solid at room temperature (m.p. = 99.5°C ; b.p. = 231°C). It has an intermediate volatility among boron hydrides (Sto33). It slowly

Table 2.5 List of Potential Boron Precursors

chemical	supplier	features
decaborane	Aldrich, Alpha	being studied at UF
1,2-carborane	Aldrich	pyrolysis gave BC (2 % yield)
borane:pyridine complex	Aldrich, Fluke	liquid; polymerization and pyrolysis gave $BC_{3.5}N$ (20-90 % yield)
borane:ammonia complex	Aldrich	crystalline solid; soluble in water, MeOH, benzene; pyrolysis gave BN (65 % yield)
carborane-siloxane copolymer	not commercially available	pyrolysis gave SiC/B ₄ C (60-70 % yield)
poly(borophenyl)-siloxane	not commercially available	pyrolysis gave SiC/B ₄ C (43 % yield)
borane:dimethyl-amine complex	Aldrich	not studied mp = 36°C; fp = 43°C
borane:poly(2-vinyl pyridine) complex	Aldrich	not studied; yellow crystalline powder; mp > 300°C; vinyl moiety fits UF approach

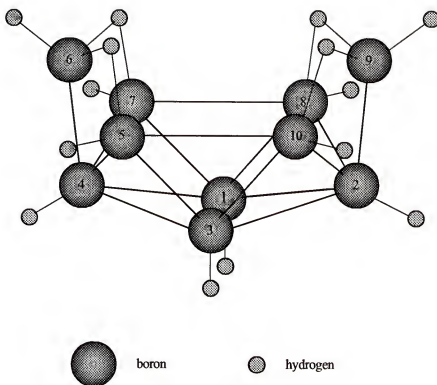


Figure 2.6 Chemical Structure of Decaborane ($B_{10}H_{14}$) (Hou90)

evaporates at room temperature and crystallizes in needle-like shape. Decaborane is relatively stable with respect to air oxidation and does not decompose even when it was stored in air or oxygen at 50 to 60°C. It has been reported that decaborane tends to decompose readily at temperatures over 150°C (Sto33).

Decaborane chemistry has been known to be very complex. It is partly due to the difference in charge distribution between boron atoms. The order of charge distribution in $B_{10}H_{14}$ is:

$$\begin{array}{ccccccc} 6, 9 & > & 5, 7, 8, 10 & > & 1, 3 & > & 2, 4 \\ 0.33 & & 0.12 & & -0.04 & & -0.10 \text{ (in electron charge)} \end{array}$$

The reaction of decaborane with weakly basic ligands such as acetonitrile was first reported in 1957 (Sch58):



In this reaction, the $B_{10}H_{14}$ cage is essentially reduced; loss of two hydrogen atoms and a gain of two 2-electron donor ligands correspond to a net gain of two cluster electrons. The weakly bonded ligand is displaced by a ligand of greater nucleophilicity (Moe76, Hou90). The displacement reaction sequence in which a ligand on the right will displace that on the left is (Moe76):



Figure 2.7 summarizes a few important reactions of decaborane.

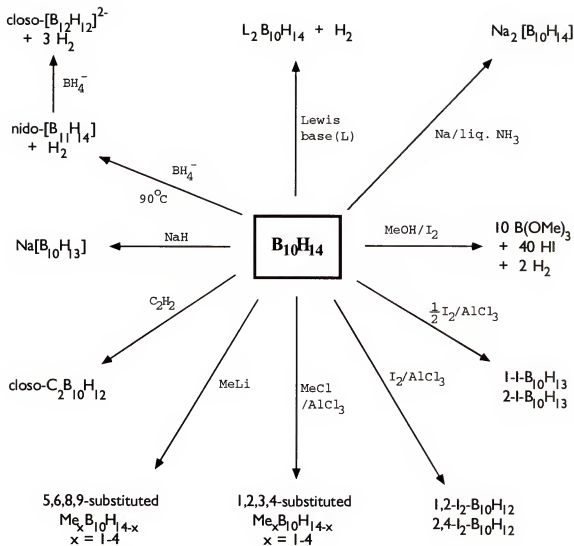


Figure 2.7 Chemical Reaction Tree of Decaborane ($B_{10}H_{14}$) (Hou90)

CHAPTER 3 EXPERIMENTAL PROCEDURE

Preliminary Study 1: Polymerization and Copolymerization

Table 3.1 summarizes the information for the chemical reagents used in the polymerization study. The silazane monomer (SZ) and the siloxane monomer (SX) were polymerized via a solution polymerization method. The copolymerization of polycarbosilane (PCS) with SZ or with SX was studied. Dicumyl peroxide (DCP) was used as a catalyst in all reactions. The PCS used mostly in this study was X9-6348, made by Nippon Carbon in Japan and distributed by Dow Corning in the United States which we designated DC PCS. Table 3.2 summarizes properties of DC-PCS.

Polymerization and copolymerization reactions were accomplished using an acid digestion bomb (Fisher Scientific 01-023). The bomb includes a polytetrafluoroethylene (PTFE) cup with a steel spring-loaded closure. The reaction conditions were predetermined from previous research at UF (Tore90) and were used for all polymerization and copolymerization reactions reported here. SZ or SX was mixed with DCP in a PTFE cup. Subsequently, the solution mixture in the PTFE cup was purged with nitrogen or argon and sealed tight by the steel spring closure. The bomb assembly was heated at 130°C in an oven for 18 hours.

After reaction, the PTFE cup was cooled to room temperature. The cup was opened and the product was visually inspected. A glass stirring rod was used to feel the

Table 3.1 List of Studied Chemical Reagents

item	silazane monomer	siloxane monomer	DCP
supplier	Huls America Inc.	PCR Inc.	Aldrich Chem. Co.
full name	1,3,5,7-tetramethyl- 1,3,5,7-tetravinyl- cyclotetrasilazane	2,4,6,8-tetravinyl- 2,4,6,8-tetramethyl- cyclotetrasiloxane	dicumyl peroxide
product #	T-2060	17119-9	32954-1
state at 25°C	liquid	liquid	white solid

Table 3.2 Properties of Dow Corning-PCS (DC92)

property	Dow Corning polycarbosilane
product name	X9-6348
appearance	pale yellow solid
melting temp (°C)	195 - 237
chemical structure	$\begin{array}{ccc} R_1 & & R_3 \\ & \text{--} [\text{Si} - \text{CH}_2 - \text{Si}]_n \text{--} \\ & R_2 & \text{H} \end{array}$
solubility	soluble in n-hexane and toluene
specific gravity	~ 1.12 at 30°C
MW (mean)	1420 - 1450
oxidation	6 - 8 w/o oxygen pick up (145 - 180°C for an hour in air)

viscosity of the products. The products were classified by their viscosity: hard gel, soft gel, gel-liquid mixture, viscous liquid, or thin liquid.

For the copolymerization, PCS was dissolved in toluene before being mixed with a monomer. The PCS solution was mixed with SZ (or SX) and DCP in the PTFE cup and the mixture was heated for reaction in an oven at 130°C for 18 hours. The products of the copolymerization were visually inspected to see if they were gelled or viscous solutions.

Non-gelled PCS-SZ copolymer solutions were processed to make powders. DCP was added in copolymer solutions to evaluate its effectiveness for crosslinking. DCP added for the copolymerization is referred to as *DCP1* while that added later to the copolymer for enhanced crosslinking is referred to as *DCP2*. The polymer solution was transferred to a round-bottom 50 ml flask for easy handling. A rotary evaporator system (Brinkmann: RotaVap) was used for drying of polymer solutions. Vacuum was provided by a rotary pump. A refrigerated circulator (Fisher Scientific: model 9500) was used for a solvent trap. The vacuum level was adjusted by controlling a valve within a range which kept the mixture solution stable; When bubbles started forming in the solution, the valve was opened and nitrogen gas of 5 psi pressure was introduced into the flask to avoid a splash. The evaporation process was continued until the solution was fully dried so that it was suitable for grinding. The dried solid was collected and ground in a mortar by hand as fine as possible. Dried copolymer powders were stored in glass vials until being used.

Two different types of specimens were prepared for pyrolysis and for characterization: powder and disk. The disks were prepared by pressing ground powder under uniaxial pressure 16,000 psi for seven minutes in a hydraulic press (Carver Lab Press: model C). A KBr disk (for FT-IR) mold was used for the preparation of disk specimens. The diameter of the disk mold was 12.7 mm. It was found that powders from some compositions made poor, fragile disks, which were easily broken during handling.

Selected powders and disks were pyrolyzed. The conditions of pyrolysis are described in a later section. Pyrolyzed disks were visually inspected for their quality. A pyrolysis yield was calculated by recording weights of powders and disks before and after pyrolysis.

Preliminary Study 2: Carbide Formation Reactions

Several metallic silicide materials whose carbides have desirable properties for high temperature applications were considered. Among potential silicide materials, selected were silicon (Si), TiSi_2 and HfSi_2 . Some properties for those materials are summarized in Table 3.3. The Si powder was acquired from Dr. Sacks research group and the particle size distribution of Si powder was measured.

Two copolymer compositions among those examined in the previous section were selected. Their compositions are summarized in Table 3.4. The contents of Si, HfSi_2 and TiSi_2 particles were 18, 18 and 20 w/o, respectively. Silicide particles were suspended in toluene prior to being mixed with PCS-SZ solution. The particle

Table 3.3 List of Silicide Particles for Carbide Reaction Study

item	Si	TiSi ₂	HfSi ₂
supplier	Dr. Sacks	Cerac	Aesar
particle size	~ 1.0 μm	325 mesh	325 mesh
storage time	several years	short	short
purity	unknown	99.5 %	99 %

Table 3.4 Copolymer Compositions of Carbide Reaction Study

studied particles	composition (w/o)				
	DC PCS	SZ	toluene	DCPI	DCP2
Si	33.7	8.5	56.2	1.1	0.6
HfSi ₂	33.8	8.5	56.4	0.8	0.6
TiSi ₂	33.8	8.5	56.4	0.8	0.6

suspension was mixed with the copolymer solution and stirred for an hour. Large particles were excluded from the mixing by taking only the easily flowing part of the suspension. The mixture solution was evaporated and ground as described previously. Disk specimens were prepared by uniaxial pressing as well.

Disks and powders were pyrolyzed at 1000°C and later heat-treated further at elevated temperatures. The pyrolysis of specimens was carried out in a tube furnace (Thermolyne: type 21100) with a temperature controller (Honeywell: UDC 2000). Some pyrolyzed specimens were later heat-treated at a high temperature: either 1300, 1400 or 1500°C. For heat-treatment at temperatures up to 1500°C, a well-insulated tube furnace (Lindberg: GS) was used. Temperature profiles of the pyrolysis and the heat-treatments are illustrated in Figures 3.1 and Figure 3.2. The atmospheres for pyrolysis and heat-treatments were nitrogen and argon, respectively. The flow rate of the gas in each tube furnace was about 20 cm³ per minute.

Powders and disks were characterized via x-ray diffraction. Prior to HT-XRD, disk specimens were pre-pyrolyzed at 800°C in nitrogen to minimize volume shrinkage problems during HT-XRD measurements. The spectra were obtained at 1300°C initially. Subsequently, the temperature was increased to 1400°C to get another XRD spectrum. A third measurement was made at 1500°C. The specimen was cooled to room temperature and a final XRD measurement was made.

Preliminary Study 3: Decaborane High-dopes Study

Boron or boron compounds are the most widely used sintering aids in the

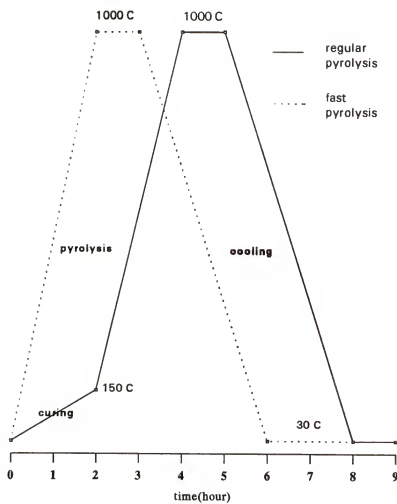


Figure 3.1 Temperature Profile of 1000°C Pyrolysis

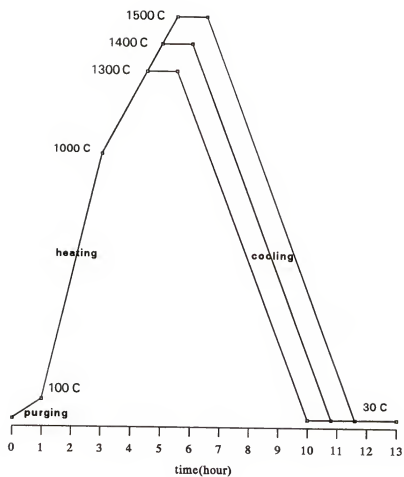


Figure 3.2 Temperature Profile of Heat-treatments

densification of SiC materials. Among the potential boron precursors, selected in this study was decaborane. Decaborane was purchased from Aldrich Chemical Company and it was weak yellow powder which was soluble in toluene and used without further purification.

Copolymers were synthesized as described previously. The copolymer compositions studied here are shown in Table 3.5. The decaborane (m.p. = 99.5°C; b.p. = 231°C) was dissolved in toluene. The copolymer solution and the decaborane solution were mixed together to make up a solution whose decaborane content was 15 w/o. The mixture was dried using a rotary evaporator. The dried mixtures were collected from the flask and ground into fine powder. For direct comparison, copolymers of the same composition without decaborane were also processed.

Interestingly enough, decaborane interacted with the silazane in PCS-SZ copolymers. As described earlier, decaborane would react with a Lewis base to fill its open cage with electron-pair donating substances. Two types of specimens were studied: powder and disk. Disks were prepared by uniaxial pressing. Specimens, after and before pyrolysis, were characterized by several techniques: weight measurement, SEM, XRD and XPS.

Fibers from PCS-based Polymers: CP Fibers

Two classes of PCS were studied: DC PCS and UF PCS. Three batches of UF PCS prepared by Dr. Toreki were used: PC143, PC144, and PC174-PCD156. DC PCS was always used in copolymers with SZ. UF PCS were used either alone or as a blend

Table 3.5 Copolymer Compositions of Decaborane High-dope Study

polymer	composition (w/o)				
	DC-PCS	SX or SZ	toluene	DCP1	DCP2
PCS-SX	30.6	10.2	57.9	0.7	0.6
PCS-SZ	32.9	3.7	62.1	0.7	0.6

with polysilazane (PSZ). DC PCS-SZ copolymers were prepared as described earlier. Fibers derived from PCS-SZ copolymer with DCP are referred to as *CP-series fibers*. The results of CP fibers are compared with those of other SiC fibers. Table 3.6 summarizes compositions and processing of CP fibers. *DC* in the table denotes DC PCS while *F3*, *F4* and *FD* stand for UF PC143, UF PC144 and UF PCD156, respectively.

PC 143 and PC144 were synthesized from polymethylsilane (PMS: Huls) by heating at around 450°C for 24 hours in an autoclave (Tor93). The pressure was initially 100 psi by nitrogen. The crude product was dissolved in toluene and filtered. PC 143 and 144 were not melted by a pyrolysis at 700°C in argon. PCD156 was derived from PDMS supplied by another manufacturer. PSZ was prepared via a solution polymerization of SZ cyclic monomer (Aldrich: T2060).

Copolymer solutions of a desired PCS/SZ ratio were mixed with DCP2. After 30 minutes of mixing, the solution was filtered using a 0.45 μm PTFE filter (Nalgene: 199-2045). The filtered solution was evaporated using a rotary evaporator to adjust the solution viscosity appropriate for fiber spinning. The solution viscosity adjustment was made solely by eye, not by any quantitative measurement.

Fiber spinning was carried out in a custom-designed spinning apparatus. Two spinnerets, obtained from DuPont company, were used for fiber spinning: one with 8 holes and the other with 4 holes. The hole sizes and the shapes were measured via SEM (see Figure 3.3). The hole diameter of the 8-hole spinneret is about 80 μm while that of the 4-hole spinneret is about 105 μm . Spinneret holes, as shown in Figure 3.3, had a little roughness.

Table 3.6 Summarized Compositions and Processing of CP Fibers

batch name	PCS (g)	SZ (g)	DCP1 (mg)	DCP2 (mg)	filter (μm)	how spun?	pyrolyzed fibers	pyrolysis yield (%)
i	4,500(DC)	0.750	100	85	0.45	good	stuck	NA
j	1,801(F4)	--	--	31	0.45	OK	OK	76.8
k	1,732(F4)	0.306	--	75	0.45	poor	OK	85.7
1	4,500(DC)	1.130	100	NA	--	OK	OK	69.5
2	4,500(DC)	1.130	100	NA	--	NA	NA	NA
3	4,500(DC)	1.130	100	85	0.1	poor	curly	71.5
4	4,500(DC)	0.930	100	85	--	poor	good	NA
5	4,500(DC)	0.750	100	85	--	poor	OK	NA
6	4,500(DC)	0.500	100	85	--	good	OK	NA
7	4,500(DC)	0.300	50	85	0.45	good	stuck	NA
8	4,500(DC)	0.300	100	85	0.45	good	curly	NA

Table 3.6 -- continued

batch name	PCS (g)	SZ (g)	DCP1 (mg)	DCP2 (mg)	filter (μm)	how spun?	pyrolyzed fibers	pyrolysis yield (%)
9	4.500(DC)	0.300	100	140	0.45	poor	OK	NA
10	4.500(DC)	0.300	50	140	0.45	poor	stuck	NA
12	4.500(DC)	0.500	100	85	0.2	good	good	68.1
13	1.805(FD)	0.320	--	80	0.45	OK	good	80.4
13P							good	NA
14	1.810(F3)	0.305	--	40	0.45	OK	good	77.7

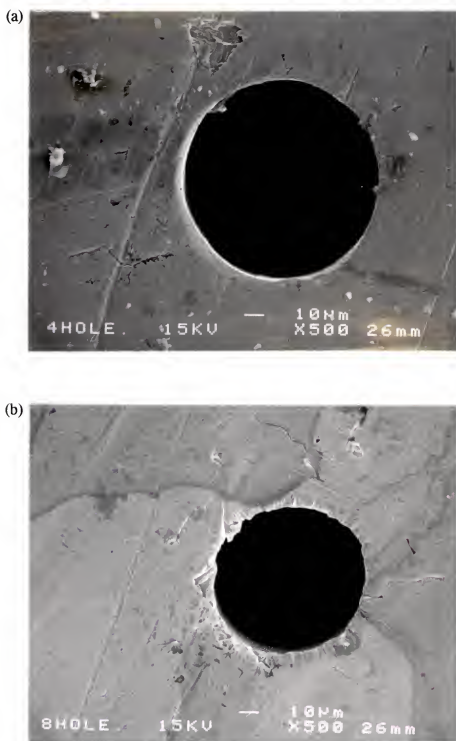


Figure 3.3 SEM Micrographs of Spinneret Holes:
(a)4-hole and (b)8-hole spinneres

The viscous mixture was transferred from a 50 ml flask into a reservoir which was attached to the spinneret. The spinning dope was forced through the spinneret by nitrogen pressure. The pressure ranged 50 to 300 psi depending on the solution viscosity. The actual viscosity was not measured. The spun fibers were wound using a spool which was connected to an electric motor. The winding speed ranged at 50 to 150 cm per second depending on the spinnability of a solution. The distance between the spinneret holes and the spool was about 35 cm. The green fibers were stored in a desiccator under vacuum until they were pyrolyzed.

The spun fibers were pyrolyzed in the tube furnace. An alundum boat (Fisher Scientific: 07-680D) was used to hold fibers during the pyrolysis. Some pyrolyzed fibers were subsequently heat-treated at elevated temperatures. The temperature cycles for the pyrolysis and the heat-treatment of fibers were shown previously. Pyrolyzed or heat-treated fibers were characterized via several analysis techniques.

Fibers from PCS-based Polymers with Decaborane: CPD Fibers

Decaborane was added to the PCS-SZ compositions and processed for fibers. Fibers derived from PCS-based polymers with decaborane incorporated are referred to as *CPD-series fibers*. *D after CP* denotes that decaborane was added to CP-series fibers. Table 3.7 summarizes compositions and processing of CPD fiber batches.

Decaborane was dissolved in toluene prior to mixing. Polymer solution of selected compositions was mixed with the decaborane solution. The mixture was left for 30 minutes. Decaborane interacted with SZ-containing polymers to turn the solution

Table 3.7 Summarized Compositions and Processing of CPD Fibers

batch name	PCS (g)	PSZ (g)	DCP1 (mg)	DCP2 (mg)	DB (mg)	how spun?	pyrolyzed fibers	pyrolysis yield (%)
i	4.500(DC)	--	--	--	55	OK	stuck	62.2
j	4.500(DC)	0.500	100	85	55	none	--	--
k	4.500(DC)	--	--	50	110	OK	stuck	69.0
1	4.500(DC)	0.270	50	50	34	poor	good	NA
2						poor	good	70.4
3	4.500(DC)	0.100	50	--	15	poor	stuck	NA
4	4.500(DC)	0.100	50	32	35	OK	stuck	61.1
5	4.500(DC)	0.160	50	51	34	none	--	--
6	4.500(DC)	0.160	50	52	34	good	stuck	63.5
7	4.500(DC)	0.160	50	100	70	poor	good	75.0
8	4.500(DC)	0.170	50	50	70	poor	curly	71.0

Table 3.7 -- continued

batch name	PCS (g)	PSZ (g)	DCP1 (mg)	DCP2 (mg)	DB (mg)	how spun?	pyrolyzed fibers	pyrolysis yield (%)
9	4.500(DC)	0.120	50	50	70	OK	good	75.2
9A							good	75.2
10	4.500(DC)	0.105	50	51	70	OK	good	72.5
10A							good	73.8
11	4.500(DC)	0.125	50	50	70	OK	good	74.3
11B						poor(B)	good	NA
13	4.500(DC)	0.500	50	50	70	poor	OK	69.2
14	4.500(DC)	0.500	50	50	70	poor	OK	70.7
15	2.007(F4)	0.113	--	50	50	none	--	--
16	1.818(F4)	0.019	--	30	50	poor	OK	73.3
17	1.811(F4)	--	--	30	60	OK	good	80.8

Table 3.7 -- continued

batch name	PCS (g)	PSZ (g)	DCP1 (mg)	DCP2 (mg)	DB (mg)	how spun?	pyrolyzed fibers	pyrolysis yield (%)
18	4.500(DC)	0.060	50	--	71	best	stuck	66.7
19	1.802(F4)	--	--	30	20	good	good	79.7
20	1.809(F4)	--	--	31	150	poor	OK	NA
21	1.802(F4)	--	--	31	151	good	good	78.6
22	1.805(F3)	--	--	32	64	poor	good	66.7
23F	1.800(FD)	--	--	80	61	poor	OK	79.7
24F	1.800(FD)	--	--	80	63	poor	OK	81.3

hazy during this time. The solution was filtered using 0.45 μm PTFE filters. The filtered mixture was exposed to an evaporation process to adjust its viscosity to be suitable for fiber spinning.

I examined if the gelation problems could be relieved by using a tertiary amine to stabilize the decaborane in the PCS-SZ compositions. The chemical used was *N,N*-diisopropyl-ethylamine (DPEA), $[(\text{CH}_3)_2\text{CH}]_2\text{-N-C}_2\text{H}_5$. Two fiber batches were prepared with DPEA incorporation: CPD13 and CPD14. For CPD13 fibers, DPEA was mixed with DB solution first and then, mixed with PCS-SZ copolymer solution. About 10 minutes after DPEA and DB were mixed, there was observed a solid phase suspended in the solution mixture. The floating solid phase was assumed to be the product of amine-borane interaction. A similar mixture with copolymer added was filtered using 0.45 μm PTFE filters and processed for fibers. In CPD14, to avoid the formation of solid phase product, DPEA was mixed with copolymer solution first and then, mixed with DB solution. Despite this precaution, the solid product was again formed (to a lesser extent) and remained suspended in the solution. In either procedure, the smell of decaborane was not noted, which means that a large part of the decaborane was either precipitated and filtered out of the solution, or bound in solution so that it was not volatile.

Fiber batches of CPD19 to CPD21 were prepared to investigate the effect of boron content in the fiber on fiber properties such as thermostability. The decaborane content in the spinning dope for CPD19 fibers was one third that in CPD17 fiber dope while the decaborane content in CPD20 and CPD21 fiber dopes was 2.5 times as much

as that in CPD17 batch. CPD20 compositions failed to make fibers due to low viscosity. CPD19 and CPD21 fibers spun well and the pyrolyzed fibers were in good shape; straight and easily separable.

The spin dopes were spun followed by the pyrolysis and the heat-treatment at elevated temperature. Some pyrolyzed fibers were additionally heat-treated at 1800 or 1850°C. A batch furnace (Centorr) with argon flow was used for the heat-treatment. The heating rate was 30 degree per minute and there was no temperature hold until the peak temperature was reached. The temperature was held for one hour at the peak temperature. Pyrolyzed or heat-treated fibers were characterized.

Fibers from PCS-based Polymers with Si Particles: CS Fibers

Fibers derived from Si-particles incorporated PCS-based polymers are referred to as the *CS-series fibers*. All fiber batches except CS12 to CS14 were prepared with DC PCS-SZ copolymers. UF PC138 was used for polymer blend solutions of CS12 to CS14 fiber batches. The Si particle content was either 14 or 25 w/o. Table 3.8 summarizes compositions and processing of CS fibers.

Figure 3.4 illustrates the overall CS fiber fabrication process. The as-received silicon particles were fractionated to collect the fine size portion. The procedure of the fractionation was established at UF in a preliminary study (Sal92). A slight modification was made to the results of that preliminary study. The 1.5 grams of a commercial dispersant (DuPont: Hypermer KD3) was dissolved in toluene of 100 grams. The 93.2 grams of Si powder was added to the KD3 solution. The solution was mixed by a paint-

Table 3.8 Summarized Compositions and Processing of CS Fibers

batch name	PCS (g)	PSZ (g)	DCP1 (mg)	DCP2 (mg)	Si content (w/o)	how spun?	pyrolyzed fibers	pyrolysis yield (%)
1	4.500(DC)	1.125	140	70	14	poor	OK	NA
2	4.500(DC)	1.125	140	70	14	OK	OK	72.2
3	4.500(DC)	1.125	140	70	14	OK	good	75.9
4	4.500(DC)	1.132	142	70	14	poor	OK	NA
5	4.500(DC)	1.130	140	70	14	poor	good	NA
6	4.500(DC)	1.132	140	100	14	good	good	70.3
7	4.500(DC)	1.130	140	100	14	poor	OK	NA
8	4.500(DC)	1.132	100	100	14	OK	good	NA
9	4.500(DC)	1.000	100	100	14	good	OK	NA
10	4.500(DC)	1.000	100	100	25	poor	stuck	NA
11	4.500(DC)	1.000	100	100	14	poor	OK	NA

Table 3.8 --- continued

batch name	PCS (g)	PSZ (g)	DCP1 (mg)	DCP2 (mg)	Si content (w/o)	how spun?	pyrolyzed fibers	pyrolysis yield (%)
12	83.8 % (F8)	13.4 %	1.6 %	--	14	poor	poor	NA
13				--	20	OK	good	NA
14				--	25	good	good	NA
15	4.500(DC)	0.500	100	85	14	poor	poor	70.4

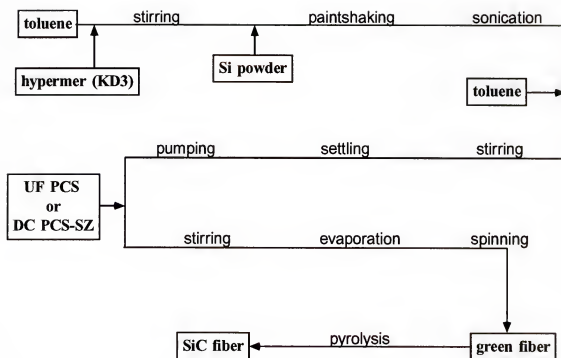


Figure 3.4 Flow Diagram of CS Fiber Processing

shaker (Red Devil: 5400) for two hours prior to the ultrasonication. Then the solution was ultrasonicated (Sonics & Materials: Vibra Cell) for two hours. The ultrasonicated solution was mixed with pure toluene in a flask to make up a 2-liter suspension. The suspension was transferred to a two-liter glass cylinder and left for settling. After 8 days of settling, the upper one liter of solution was removed using a suction pump (Milpore). The particle size distribution of the fractionated Si solution was measured using a particle size distribution analyzer (Horiba CAPA 700).

The copolymers were prepared as described previously. The copolymer solution was mixed with the fractionated Si solution to make a mixture whose Si content was 14 or 25 w/o. The volume of the mixture ranged from 200 to 500 ml depending on the Si content. The solvent in the solution was removed via evaporation until the viscosity of the mixture was appropriate for fiber spinning. The Si-incorporated polymer solutions were opaque in brown color compared to the clear solutions of CP and CPD fiber dopes. Since the solution viscosity was approximately measured by visually inspecting the solution's flowability through the flask wall, final viscosity adjustment was rather difficult for CS fiber dopes. Fiber spinning, pyrolysis at 1000°C and subsequently heat-treatment at elevated temperatures were performed as described previously, followed by various characterizations.

An attempt was made to wash as-received Si particles and as-pyrolyzed CS fibers in strong acids. Concentrated HF or HF-H₂SO₄ solutions were used. Si particles were washed in the concentrated HF (~50%) hopefully to remove the Si-O_x layer on the particle surface. Due to a severe flocculation occurring right after Si particles were in contact

with the acid, cleaning this way was discontinued. Even a few grams of Si particles caused a flocculation in about a hundred grams of acid. No further effort to clean Si particles has been made since. The as-pyrolyzed fibers were treated in four different ways followed by a heat-treatment at 1500°C: (a) none, (b) acid wash only, (c) boric acid dipping only and (d) acid wash and boric acid dipping. The cleaning acid was prepared by mixing HF with H_2SO_4 in 1:1 volume ratio in a PTFE beaker. The washing progressed for 4 days at room temperature. Boric acid was prepared by dissolving B_2O_3 (boric anhydride) powder in distilled water up to saturation. The exact solution concentration of the boric acid was not measured, but a reference (Mer89) suggested that the solubility of B_2O_3 in cold water is 30 ppm. Fibers after either treatment were heat-treated at 1500°C and characterized.

Fibers from PCS-based Polymers with Si particles and Decaborane: CSD Fibers

Decaborane was added to the CS fiber compositions. DC PCS and two UF PCS were used. Fibers from PCS copolymers with Si particles and decaborane are referred to as *CSD-series fibers*. The same interactions, between decaborane and PCS-SZ copolymers as in CPD batches, were observed. The fiber processing procedure for CSD fibers is exactly the same as that for CS fiber, except adding decaborane in CSD fiber and somewhat adjusting SZ content for DC PCS polymers. Table 3.9 summarizes compositions and processing of CSD fibers.

Other Fibers 1: Fibers from PCS-SX Polymers with/without Decaborane: CY Fibers

DC PCS-SX copolymers were used to make fibers, instead of DC PCS-SZ copolymers. SX incorporation was used to introduce more oxygen than SZ provided into fibers. PCS-SX copolymers were prepared exactly the same as PCS-SZ copolymers. Fibers derived from PCS-SX copolymers with/without decaborane are referred to as *CY-series fibers*. Si particles were incorporated along with decaborane in CY4 fibers. Table 3.10 summarizes compositions and processing of CY fiber batches.

Other Fibers 2: Fibers from PCS-SZ Polymers with SiC Particles: CX Fibers

Silicon carbide particles, instead of Si particles, were incorporated in making SiC fibers. Fibers from DC PCS-SZ copolymers with SiC particles are referred to as *CX-series fibers*. Two SiC powders were studied: α -SiC and β -SiC. Decaborane was not added to any CX batches. For CX1, α -SiC particles were used while for CX2 and CX3, β -SiC particles was employed. The α -SiC particles were acquired from Dr. Sacks' research group. The particle fractionation procedure was described earlier. The α -SiC particles were known to be aged several years. The fractionation of the particle was without difficulty and the α -SiC particle suspension was mixed with PCS-SZ copolymer after being settled for two weeks.

The β -SiC particles were newly purchased from Alpha Chemical Company. A particle fractionation was not well behaved using the Si particle settling conditions. β -SiC particle solution was mixed with copolymer solution after a settling of one hour. Table 3.11 summarizes compositions and processing of CX batches.

Table 3.10 Summarized Compositions and Processing of CY Fibers

batch name	PCS (g)	PSZ (g)	DCP1 (mg)	DCP2 (mg)	DB (mg)	Si content (w/o)	how spun?	pyrolyzed fibers	pyrolysis yield (%)
1	4,500(DC)	0.80	100	88	31	--	NA	OK	76.8
2	4,500(DC)	0.60	100	85	--	--	good	good	65.1
3	4,500(DC)	2.00	100	80	--	--	NA	OK	69.0
4	4,500(DC)	0.60	100	23	23	14	poor	OK	NA

Table 3.11 Summarized Compositions and Processing of CX Fibers

batch name	PCS (g)	PSZ (g)	DCP1 (mg)	DCP2 (mg)	DB (mg)	SiC content (w/o)	how spun?	pyrolyzed fibers	pyrolysis yield (%)
1	4,500(DC)	0.575	100	80	--	30	OK	good	76.8
2	4,500(DC)	0.270	50	88	--	14	OK	stuck	69.8
3	4,500(DC)	0.270	50	100	70	14.	OK	OK	75.8

Characterization of Materials

The processed fibers were characterized via several techniques: tensile testing, density, scanning electron microscopy (SEM), x-ray powder diffraction (XRD), transmission electron microscopy (TEM), scanning Auger spectroscopy (SAM), x-ray photoelectron spectroscopy (XPS), and neutron activation analysis (NAA).

The tensile testing of fibers was based on ASTM D3379-75 (AST82). Figure 3.5 illustrates a schematic diagram of a mounted specimen for tensile testing. A single fiber strand was mounted on a paper tab and was permanently glued to it by epoxy (Duro Master Mend) or wood glue (Franklin Titebond). The mounted fiber specimen was held tight by a pneumatic grip at an air pressure of 40 psi. The alignment of fibers was examined visually and adjusted. Fiber specimens were left for curing overnight before being tested. The diameter of fibers were measured via an optical microscope (Nikon). Each fiber was measured at two points for the diameter at one thousand magnification.

The supporting edges of the paper tab were cut to insure that all tension was transferred to the fibers. The distance between the two grips was 3.2 cm. An Instron 1122 with a 500 gram load cell (Instron 2511-101) was used. The specimen was pulled at 0.02 inch per minute. All tests were conducted at room temperature and room humidity. Test results were recorded on chart paper. A maximum load and an elongation at break were measured and the tensile strength (TS), elastic modulus (EM) and rupture strain (RS) were calculated from those numbers. For some of most recent fiber batches, a personal computer was used for the supplementary acquisition of data. These two methods had given very similar results.

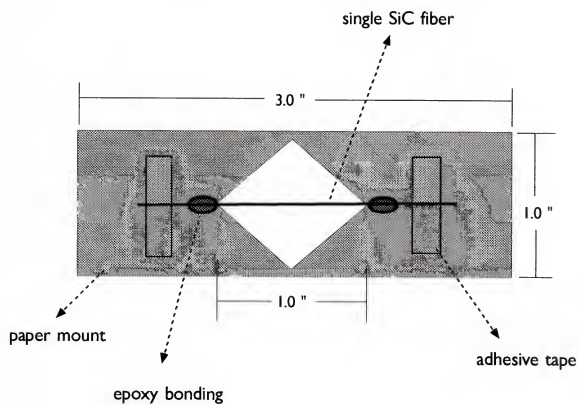


Figure 3.5 Schematic Diagram of Fiber Specimen for Tensile Testing

The topography of fiber surfaces and fractured cross-sections was measured via SEM. The later fiber batches were studied via a new SEM (JEOL JSM-6400), which has a better resolution capability than SEM (JEOL CF35). A carbon paste (SPI #5006) was used not only to fix the fibers on the aluminum mount but also to enhance the electrical conductivity. The specimens were coated with gold-palladium in a sputter coater (Technics: Hummer V). The acceleration voltage of the electron gun was 15 kV. When there was a severe charging problem, the acceleration voltage was decreased to 10 kV. Two SEM pictures were taken for each fiber (which was presumably representative) at about 3,000 and 20,000 times magnification. Polaroid 4 x 5 instant sheet films (professional 55) were used. An energy dispersive spectrometer (EDS: Tracor Northern) was attached to the JSM-6400 SEM.

The crystallographic information for the fibers was obtained via powder x-ray diffractometry (XRD). Two XRD instruments (Philips: APD 3720) were employed. One was the regular XRD for measurement at room temperature (RT-XRD) and the other was an XRD which has a hot stage capable of generating temperatures up to 1550°C (HT-XRD). Since the sample stage is moving along with the Bragg angle change, only disk specimens were analyzed by the HT-XRD. Therefore, HT-XRD was used only for the carbide reaction study. The disk was fixed on a shallow lip of a tantalum strip. The desired temperature was attained by heating the tantalum strip by the resistance. Argon was flowing (about 5 cm³ per minute) in the HT-XRD during the heating. The heating rate with HT-XRD was extremely fast (~100°C per minute). For RT-XRD, the powder was mounted on a provided glass plate using double-stick tape. The area of the specimen

was about 10 x 10 mm. Scanning was performed in continuous mode where the scanning speed was set as 0.05 degree per second. The XRD spectrum for each specimen was obtained for 2θ of 20 to 80 degrees.

Scanning Auger microscopy (SAM) was performed using a PHI Perkin-Elmer 660 microprobe. 10 keV electrons at a total beam current of 0.05 μA were used with a beam diameter of about 0.5 μm . For a depth profile, the specimen was sputtered with a small dose of 3 keV argon ions. After an SED image for a desired area was generated by rastering the electron beam, a survey scan for the kinetic energy of 0 to 1000 eV was conducted. Then, narrow scans of detected elements were performed.

A Perkin-Elmer 6000 series spectrometer was used to obtain x-ray photoelectron spectra. A magnesium x-ray tube which emits a 1253.4 eV x-ray was used. No electron flood gun was used because there was no monochromator in the XPS. Since the XPS is operating with a sample of large size under an ultra-high-vacuum (UHV), only well-densified flat specimens are measured. Therefore, only pyrolyzed disks in the decaborane high-dope study were analyzed via XPS.

Detailed morphology and the electron diffraction spectra for fibers were obtained via TEM. JEOL 200CX (maximum 200 kV) and 4000FX (maximum 400 kV) instruments were employed. Particle size information was obtained via a particle size distribution analyzer (Horiba CAPA-700). Calibration was conducted with pure toluene and measurements were made with very dilute solutions of particles in toluene. The surface area of fibers was measured via a BET instrument (Micromeritics ASAP 2000).

The density of fibers was measured based on ASTM D3800-79 (AST85); procedure B: Sink-float technique. Two chemical solvents were used: carbon tetrachloride (CCl_4 ; $\rho = 1.585 \text{ g/cm}^3$ at 23°C) and methylene iodide (CH_2I_2 ; $\rho = 3.325 \text{ g/cm}^3$ at 23°C). About 5 grams of CCl_4 and about 10 grams of CH_2I_2 were mixed in a 20 ml glass scintillation bottle: The actual amount of each solvent was recorded and the starting density is about 2.43 g/cm^3 . The mixture was sonicated for 30 seconds. In each bottle, three fragments (about 1 cm long each) of fibers were introduced. The mixture bottle was sonicated for another 30 seconds. Then, the bottle was left in a thermostat at 23°C for 30 minutes before it was taken out and inspected for the location of fibers.

If the fibers sank down on the bottom, about 3 grams of CH_2I_2 was added to increase the density of the mixture. If the fibers were floating on the surface of the mixture, about 6 grams of CCl_4 was added to decrease the density. These additions of either solvent were repeated until the fibers were suspended at an intermediate point, where the density of fibers is regarded to be the same as that of the mixture. The density was measured by two methods: by mixture composition and by pycnometer. The first method was to calculate the density using the following simple equation:

$$\rho_{\text{comp}} = \frac{\text{wt of mixture}}{\frac{\text{wt of CCl}_4}{1.585} + \frac{\text{wt of CH}_2\text{I}_2}{3.325}}$$

A glass pycnometer (CAMEOS 20 ml) was used for the second method. The mixture was cooled to 23°C before being measured. The cleaned, empty pycnometer was weighed at 23°C . The pycnometer was filled with the mixture followed by wiping and removing bubbles. The pycnometer with the mixture was weighed when the

temperature reached 23°C. The density by pycnometer was calculated using the following equation:

$$\rho_{pyc} = \frac{wt\ of\ pycnometer+mixture - wt\ of\ pycnometer}{vol.\ of\ pycnometer\ (=9.77264)}$$

Neutron activation analysis (NAA) was used to obtain a quantitative measurement of the elemental compositions of the fibers. All NAA work was conducted by radio-analytical service department at the University of Kentucky. Silicon and oxygen were analyzed for each specimen.

CHAPTER 4

RESULTS AND DISCUSSION

Preliminary Study 1: Polymerization and Copolymerization

The objectives of this part were to examine the predetermined solution polymerization conditions (by heating at 130°C for 18 hours) to prepare polysilazane (PSZ), polysiloxane (PSX) and polycarbosilane-silazane (PCS-SZ) copolymers and to find compositions which give products with appropriate rheological properties such as viscous solutions. DC PCS was used for the copolymerization. Compositions determined in this section were reproduced to prepare polymer or copolymer solutions for the carbide reaction and fiber studies.

There were two variables in the polymerization study: the ratio of monomer (SZ or SX) to toluene and the amount of DCP. Figure 4.1 and Figure 4.2 illustrate composition diagrams for the polymerization of SZ and SX, respectively. There was a boundary to differ the compositions of gelation from those of the viscous region in each diagram. The estimated boundary was denoted by a dotted line. When compositions were very close to the boundary in the solution region, polymerization products were very viscous solutions, which were gelled after a short period of storage. When compositions were apart from the boundary, products were a very thin liquid in the solution region and hard gel in the gelation region. It was clear that a low toluene content or a high DCP content tended to cause gelation. SZ needed more toluene than

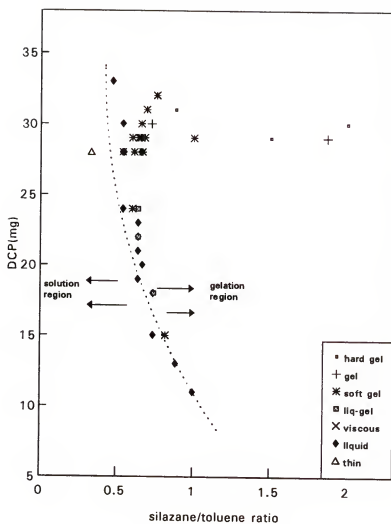


Figure 4.1 Composition Diagram of Silazane Polymerization

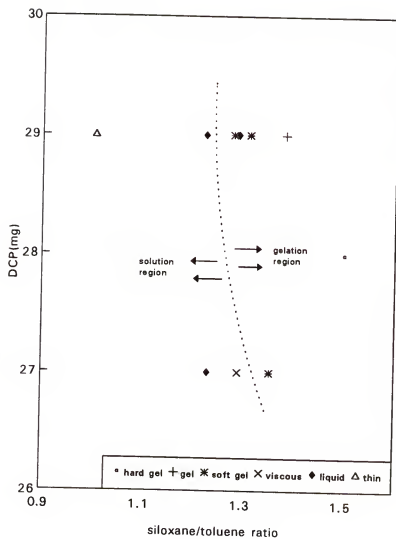


Figure 4.2 Composition Diagram of Siloxane Polymerization

SX to give solution products. The polymerization compositions were well reproducible. Detailed characterization of products using a gel permeation chromatography (GPC) was not performed.

The ratio of PCS to SZ and the amount of DCP were taken into account as variables in the copolymerization study. Figure 4.3 shows the composition diagram for DC PCS-SZ copolymerization. Similar to polymerization composition diagrams, there was a boundary between the solution and gelation regions. It was found that solution products whose compositions were close to the boundary were easily gelled after being stored in a vial for several hours. This was assumed to be due to the incorporation of oxygen into polymer chains.

Preliminary Study 2: Carbide Formation Reactions

XRD analysis was employed to monitor the reactions between silicide and the polymer dope. Silicide particles were incorporated and it was known that carbon was present in excess in the UF PCS-derived SiC materials. Figures from 4.4 to 4.11 summarize results from RT-XRD and HT-XRD analysis. Crystalline phases of Si, HfSi₂, TiSi₂, SiC, HfC and TiC were detected via XRD. The peak heights were read in terms of the number of counts and used for a semi-quantitative comparison. The JCPDS handbook (JCP88) was referred to for the reference XRD data.

Figure 4.4 shows the change of XRD patterns of PCS-SZ copolymer without particles with respect to the heat-treatment temperature. No apparent peaks were detected via XRD before and after a 1000°C pyrolysis. Therefore, not only copolymers

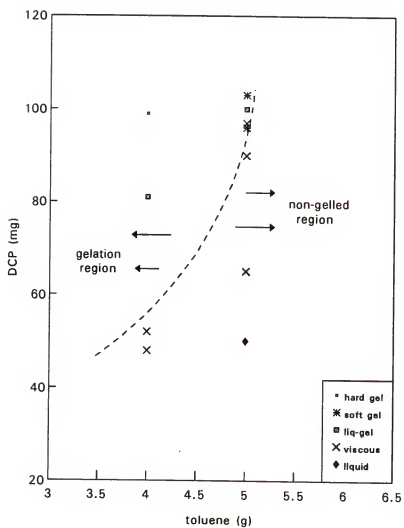


Figure 4.3 Composition Diagram of DC PCS-Silazane Copolymerization

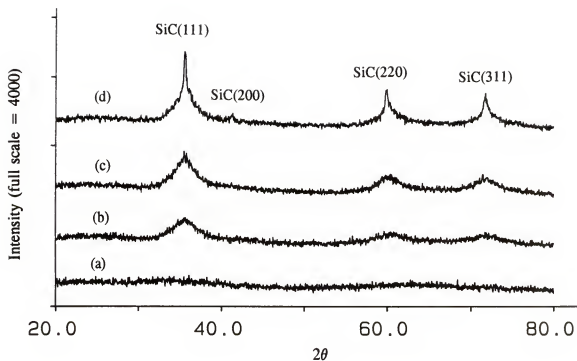


Figure 4.4 X-ray Diffraction Patterns of PCS-SZ Polymer: Effect of Heat-treatment Temperature (a) before Pyrolysis, (b) after 1300°C Treatment, (c) after 1400°C Treatment and (d) after 1500°C Treatment

but pyrolyzed SiC materials were all amorphous. After 1300°C treatment, three broad peaks were formed. As the treatment temperature increased up to 1500°C, those peaks grew up to large ones. The three peak positions were $2\theta = 35.6, 60.0$ and 71.8° . A small shoulder was formed at $2\theta = 41.4^\circ$ after a 1500°C treatment. Those peaks correspond to crystalline β -SiC of (111), (220), (311) and (200) directions, respectively. The crystalline size and the degree of crystallinity increased as the specimen was treated at elevated temperatures.

Figure 4.5 illustrates the XRD patterns of the mixture of PCS-SZ copolymer and Si particles. Five peaks were detected for the mixture before the pyrolysis [see Figure 4.5(a)]: $2\theta = 28.5, 47.3, 56.1, 69.2$ and 76.4° . Those peaks corresponded to crystalline silicon of (111), (220), (311), (400) and (331) directions, respectively. A 1000°C pyrolysis did not change the XRD patterns. After 1300°C treatment, three broad peaks were formed as shown in Figure 4.5(b). The peak heights were almost the same as those for SiC in Figure 4.4(a). Therefore, there was not either additional formation of SiC or a change of crystallinity in Si particles by 1300°C treatment. After a 1400°C treatment, peaks for β -SiC grew up to large ones while peaks for Si became smaller. The peak intensity of SiC was comparable to that after a 1500°C treatment in Figure 4.4(d). Therefore, there was a progress of carbothermal reaction between the incorporated Si particle and excess carbon to produce SiC:



Peaks for Si disappeared and peaks for SiC grew very sharp after 1500°C treatment, as shown in Figure 4.5(d). This means that incorporated Si particles were all consumed for

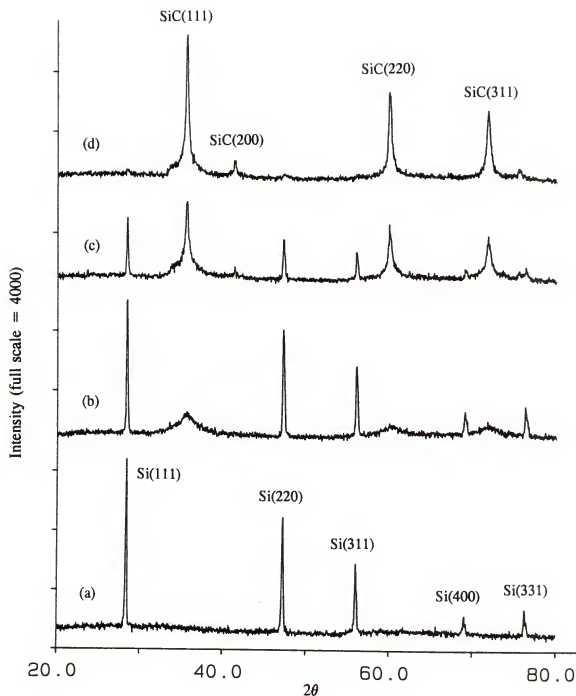


Figure 4.5 X-ray Diffraction Patterns of a Mixture of PCS-SZ Polymer and Si Particles: Effect of Heat-treatment Temperature (a) before Pyrolysis, (b) after 1300°C Treatment, (c) after 1400°C Treatment and (d) after 1500°C Treatment

the reaction. Some portion of the large SiC peaks was attributed to the SiC phase produced by the carbothermal reaction. It seemed that, since the melting temperature of silicon is about 1410°C, the reaction was activated only when the temperature was close to or over 1400°C.

A recent study (Wan91) showed that the reaction between silicon and carbon (graphite) is appreciable when the reaction temperature was over the melting temperature of silicon, 1410°C. Findings from our following results appeared to show that this is not true. The mixture powder was heat-treated at 1400°C for an hour under argon, but with one hour holding at 1000°C. This was to see the effect of a change in temperature profile on the reaction progress. XRD patterns of two specimens treated at 1400°C, one without a hold at 1000°C and the other with an hour holding at 1000°C, are shown in Figure 4.6. Si particles were consumed more and peaks for SiC became larger by having one hour holding at 1000°C. These results indicated that the reaction is a kinetic process whose extent of progress depends upon several other factors beside the peak temperature. Hence, sample size, spatial distribution of incorporated particles, temperature profile, purity and other factors will be significant. The reaction might have gone to completion by holding the specimen for several hours at 1000°C before being treated at 1400°C.

For a HT-XRD measurement, a disk specimen was mounted on a tantalum strip, which also gave a few peaks itself to cause some superimposition problems in the analysis of XRD patterns. The actual HT-XRD patterns are not shown here, but summarized results are given in Figure 4.7. Four non-superimposing four peaks of Si and SiC were measured for their intensity changes with respect to the treatment

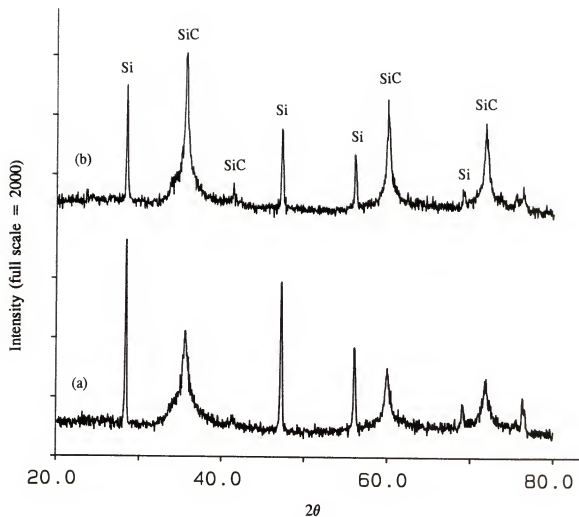


Figure 4.6 X-ray Diffraction Patterns of a Mixture of PCS-SZ Polymer and Si Particles: Effect of Temperature Profile during 1400°C Treatment (a) with no hold at 1000°C and (b) with one hour hold at 1000°C

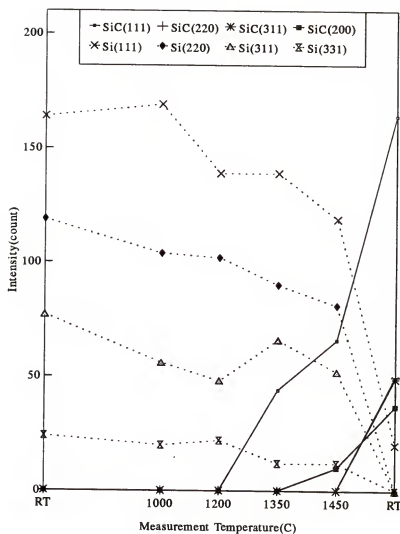


Figure 4.7 HT-XRD Peak Intensity Change of a Mixture of PCS-SZ Polymer and Si Particles

temperature. Intensity of Si peaks was reduced gradually as the treatment temperature increased to 1450°C. The specimen was heated to 1500°C where the heat controller of HT-XRD became unstable. Therefore, a measurement at 1500°C was aborted and the heating system was shut off. The specimen was cooled to room temperature and XRD pattern was measured. No measurement was made at 1500°C. Compared to those measured at 1450°C, XRD patterns at final room temperature showed much reduced Si peak intensity and greatly increased SiC peak intensity. This means that when the heating rate was extremely high as in HT-XRD measurement, the carbide formation reaction would not proceed substantially until the temperature reached 1450°C. This indication was consistent with that from the RT-XRD. Beside the temperature profile, the peak temperature seemed to be an important factor for the extent of reaction especially when the heating rate was extraordinarily high.

Mixtures of DC PCS-SZ copolymers and HfSi_2 particles were prepared and studied in the same way. Figure 4.8 summarizes the results of RT-XRD measurements with respect to the treatment temperature. Many peaks showed up when the mixture was measured before pyrolysis. Those peaks corresponded exactly to ones obtained from as-purchased HfSi_2 particles. The peaks did not match any of crystalline HfSi_2 listed in JCPDS handbook. The HfSi_2 particles used might be a mixture of several hafnium silicides. Two crystalline phases were expected to form by the reactions:



The progress of the reactions was monitored by two sets of peaks for SiC and HfC.

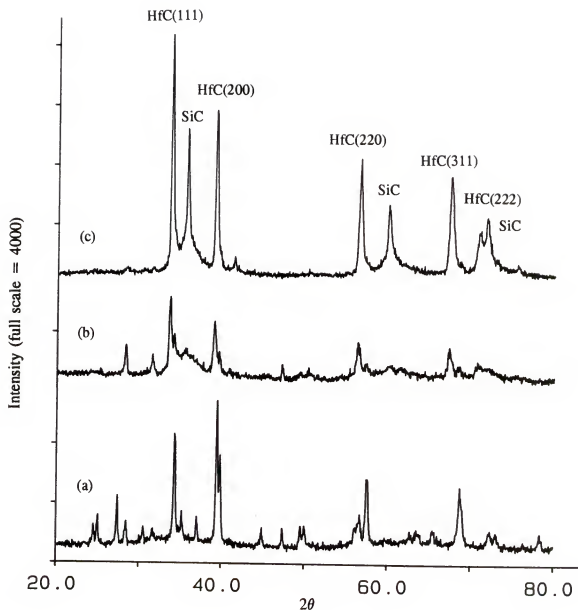


Figure 4.8 X-ray Diffraction Patterns of a Mixture of PCS-SZ Polymer and HfSi_2 ; Effect of Heat-treatment Temperature (a) before Pyrolysis, (b) after 1300°C Treatment and (c) after 1500°C Treatment

After 1500°C treatment, eight large peaks appeared in the XRD spectrum as shown in Figure 4.8(c). Peaks at $2\theta = 35.6, 60.0$ and 71.8° correspond to SiC crystalline of (111), (220) and (311) directions, respectively. Peaks at $2\theta = 33.4, 38.8, 56.0, 66.8$ and 70.2° corresponded to crystalline HfC of (111), (200), (220), (311) and (222) directions, respectively. In the spectrum obtained after 1300°C treatment [Figure 4.8(b)], broad peaks for crystalline SiC and HfC as well as few peaks for HfSi₂ particles were observed. The reaction did not proceed much after 1300°C treatment, while much of HfSi₂ particles were consumed after 1500°C treatment. Compared to the melting temperature of HfSi₂ (1680°C) and the reaction of Si particles, the reaction occurs relatively at low temperatures. This might be related to the diffusion behavior characterized by the bonding characteristics.

Figure 4.9 summarizes the results from HT-XRD analysis. There was no problem in the controller so that the specimen was measured at 1500°C before being measured at room temperature again. The reaction seemed to be appreciable when the temperature was higher than 1350°C. However, it did not proceed much by a treatment at 1500°C. This trend was not very consistent with that observed from RT-XRD analysis in that the carbothermal reaction was complete after 1500°C treatment in a tube furnace.

Figure 4.10 summarizes the XRD pattern change for the mixture of copolymer and TiSi₂ particles with respect to the treatment temperature. Eight peaks were observed in the pattern of the mixture before pyrolysis, as shown in Figure 4.10(a). Peaks at $2\theta = 30.0, 39.1, 42.2, 43.2, 49.7, 67.2, 68.7$ and 71.9° correspond to crystalline TiSi₂ of (220), (311), (040), (022), (331), (351), (313) and (620) directions, respectively. The

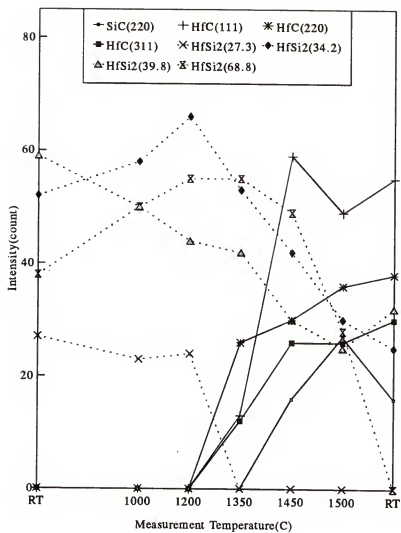


Figure 4.9 HT-XRD Peak Intensity Change of a Mixture of PCS-SZ Polymer and HfSi₂ Particles

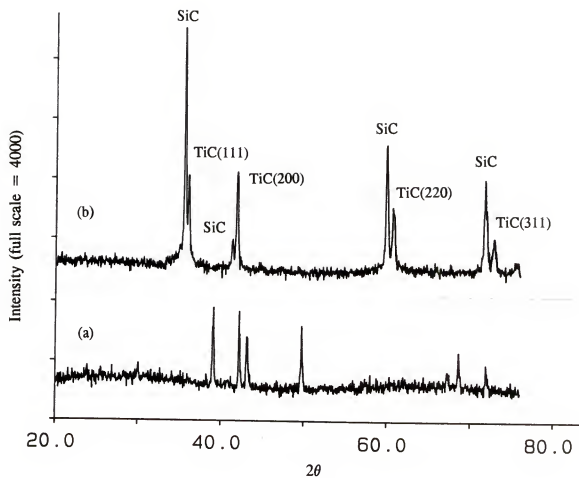


Figure 4.10 X-ray Diffraction Patterns of a Mixture of PCS-SZ Polymer and TiSi_2 : Effect of Heat-treatment Temperature (a) before Pyrolysis, (b) after 1500°C Treatment

purchased TiSi_2 particles turned out to be pure TiSi_2 according to XRD. The intended reactions between TiSi_2 particles and excess carbon were:



TiSi_2 particles remained unreacted after a 1300°C treatment (XRD spectrum is not shown). After 1500°C treatment as shown in Figure 4.10(b), TiSi_2 particles were consumed in the reaction. Eight large peaks were observed after 1500°C treatment. SiC and TiC crystalline have four major peaks very nearby. Peaks at $2\theta = 35.6, 41.4, 60.0$ and 71.8° represent the existence of crystalline β -SiC. Peaks at $2\theta = 35.9, 41.7, 60.5$ and 71.4° correspond to crystalline TiC of (111), (200), (220) and (311) directions, respectively. Considering the melting point of TiSi_2 (1720°C), the reaction tends to proceed at a relatively low temperature.

Figure 4.11 summarizes the results from HT-XRD analysis. The reaction appeared to progress to a great extent when the specimen was heated over 1350°C . When it was heated at 1500°C , only a small portion of TiSi_2 particles remained unreacted. TiC was formed when the temperature was higher than 1350°C .

Summarizing the results from the reaction study of three silicide particles, carbide formation reactions occurred well below the melting temperature of each silicide. Considering that all mixtures were prepared with as-purchased particles of large size (1 to $40\text{ }\mu\text{m}$), if much finer (submicron size) particles can be incorporated, the reactions would be expected to be completed at even lower temperatures than those observed here.

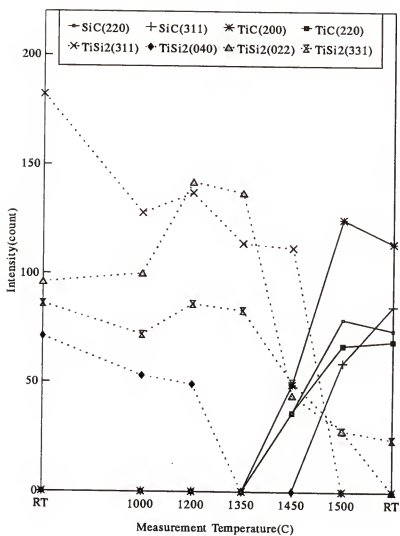


Figure 4.11 HT-XRD Peak Intensity Change of a Mixture of PCS-SZ Polymer and TiSi_2 Particles

Preliminary Study 3: Decaborane High-Dope Study

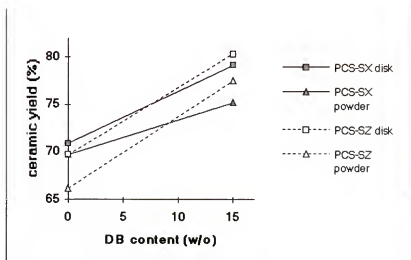
The effect of decaborane incorporation on the ceramic yield of DC PCS-based copolymers after 1000°C pyrolysis was measured. Two types of specimens were prepared: powder and disk. Table 4.1 summarizes the results of weight measurements. Numbers denote ceramic yields in weight per cent. Ceramic yields of either copolymers without decaborane were rather low (66 to 71%). Decaborane incorporation tends to increase the ceramic yield by 6 to 11%. The yield with decaborane was as high as 80%, which is comparable to that of high molecular weight UF PCS. Two possible mechanisms were responsible for the increased yields: decaborane itself had a high ceramic yield and/or the infusibility of copolymer precursors were increased remarkably by decaborane incorporation.

Decaborane is believed to vaporize rather than convert to ceramic structure by a pyrolysis process. The ceramic yield of decaborane alone, through a pyrolysis at 1000°C under nitrogen, was almost zero. TG/DTA profiles were obtained to investigate the physical and chemical change during the pyrolysis. Two temperature profiles were considered: regular pyrolysis and fast pyrolysis. A platinum pan was used to hold specimen powder. The smallest gas (nitrogen) flow rate in the instrument was 60 cm³/min, which is about three times larger than that for the fiber pyrolysis process in the tube furnace.

Figure 4.12 (a) and Figure 4.12 (b) show TG/DTA results for temperature profiles of the regular pyrolysis and the fast pyrolysis. In Figure 4.12 (a), TG percent of decaborane dropped very abruptly when the temperature reached 60°C. When the

Table 4.1 Summarized Results of Ceramic Yield Measurements:
after 1000°C Pyrolysis

sample name	ceramic yield (%)	
	disk	powder
PCS-SX (15% borane)	79.1	75.2
PCS-SX	$70.9 \pm 0.1(2)$	69.7
PCS-SZ (15% borane)	80.3	77.5
PCS-SZ	69.7	66.2



(a)

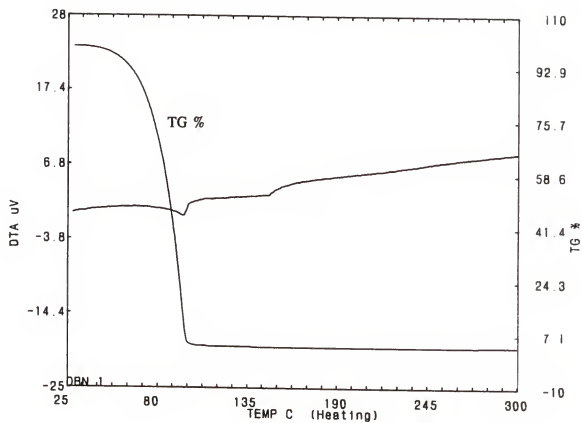


Figure 4.12 TG/DTA Results of Decaborane to 1000°C: (a) Regular Pyrolysis Temperature Profile and (b) Fast Pyrolysis Temperature Profile

(b)

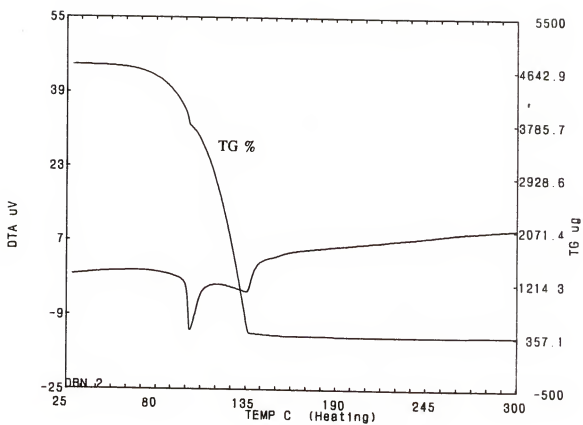


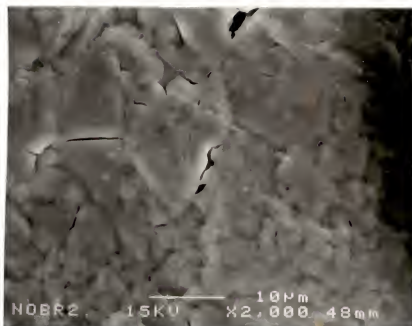
Figure 4.12 .. continued

temperature reached 100°C, the TG percent curve leveled off. The residual TG percent was measured to be 3.5%. On the other hand, in Figure 4.12 (b), TG percent dropped when the temperature was between 95 and 137°C. The residual TG percent was about 8%. A fast pyrolysis resulted in a slightly greater ceramic yield than a regular pyrolysis. A maximum heating rate (30°C per minute) of the instrument was used to examine if the ceramic yield could be further increased. The measurement was aborted due to a bubbling problem. Black spots formed possibly by a reaction between decaborane and the platinum pan. TG/DTA profile was not obtained due to instrumental problems. The above results seem to say that a fast heating rate is desirable when decaborane-incorporated fibers are pyrolyzed. By sustaining the decaborane at the maximum temperature, there should be a better chance for the conversion to ceramic compounds.

It was examined if decaborane incorporation might make a significant difference in the microstructure of pyrolyzed (at 1000°C) disks. Figure 4.13 illustrates SEM micrographs of surfaces of pyrolyzed disks with and without decaborane. Both disks have a rather dense microstructure and no topographical difference was appreciated.

Powders, before and after pyrolysis, were measured via XRD. Figure 4.15 illustrates XRD patterns of DC PCS-SX polymer powders with and without decaborane. Figure 4.14 shows the XRD pattern of an as-purchased decaborane powder. The existence of decaborane can be recognized by a peak at $2\theta = 15.0^\circ$. PCS-SX copolymer after 1000°C pyrolysis did not have any appreciable XRD peaks and obtained one broad peak near at $2\theta = 35.6^\circ$, which corresponded to SiC (111). The mixture of PCS-SX copolymer and decaborane, surprisingly did not have a peak for decaborane. There was

(a)



(b)

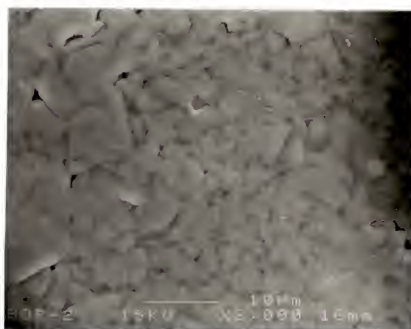


Figure 4.13 SEM Micrographs of Pyrolyzed Decaborane High-dope Disks: (a) without Decaborane and (b) with Decaborane (15 w/o)

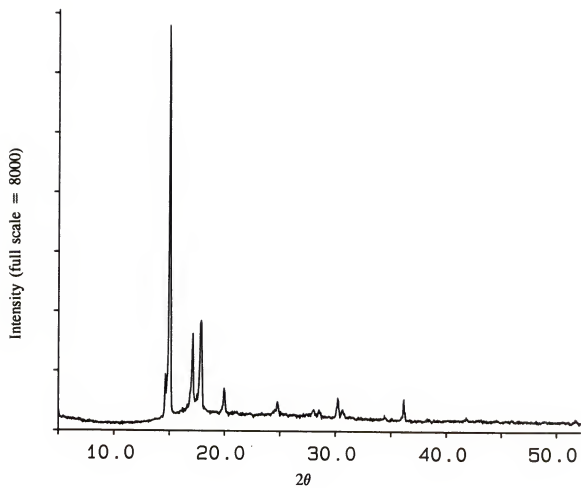
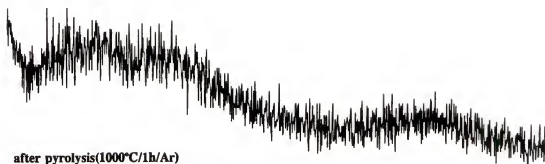
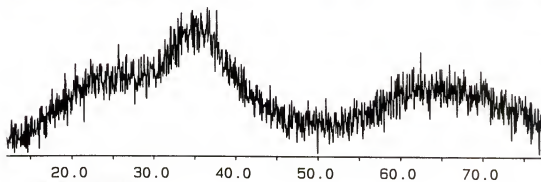


Figure 4.14 X-ray Diffraction Patterns of As-purchased Decaborane

(a) before pyrolysis

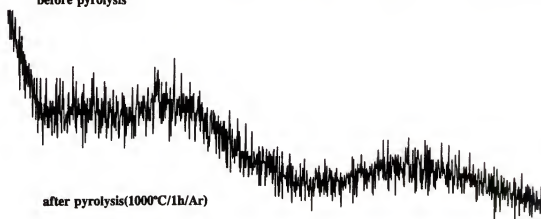


after pyrolysis(1000°C/1h/Ar)



before pyrolysis

(b)



after pyrolysis(1000°C/1h/Ar)

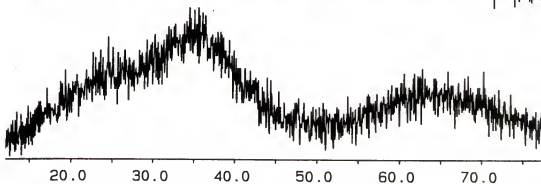


Figure 4.15 X-ray Diffraction Patterns of (a) PCS-SX Polymer and (b) Decaborane High-dope PCS-SX Polymer, before and after 1000°C Pyrolysis

no difference in the XRD patterns, made by decaborane incorporation. It was speculated that decaborane vaporized to a great extent during the evaporation process.

Figure 4.16 shows XRD patterns of PCS-SZ copolymers with and without decaborane. Similar to Figure 4.15 for PCS-SX mixture, there is no apparent effect of decaborane incorporation on XRD patterns. The only difference was that decaborane produced a sharp peak at $2\theta = 26.3^\circ$ in the unpyrolyzed mixture. JCPDS suggested this peak might correspond to the existence of B-N type crystalline phase. This peak was not matched by XRD peaks for any boron carbides or oxides suggested by JCPDS. The peak was reproduced in a duplicate XRD measurement.

Pyrolyzed disks were measured via XPS. Two measurements were made for each sample: one for as-received surface and the other for surface after 100 minute of argon ion sputtering. Figure 4.17 and Figure 4.18 illustrate XPS wide scan spectra of PCS-SX and PCS-SZ high-dope disks after 1000°C pyrolysis. Four elements were detected: carbon, oxygen, silicon and boron. The B 1s peak in the PCS-SZ high-dope disk has a greater intensity than that of the PCS-SX high-dope disk. From narrow scans of those elements, atomic concentration and peak width were measured. Table 4.2 summarizes atomic concentrations and peak areas. The oxygen content of every specimen was very high. This was surprising because PCS and SZ theoretically do not contain oxygen while SX and DCP have a low content of oxygen. Oxygen content over 50 atomic % was probably caused by a severe contamination during sample handling or pyrolysis. Ar⁺ sputtering for 100 minutes did not reduce the oxygen content significantly. This fact implied that oxygen was spread in each specimen to some depth, possibly even to the bulk.

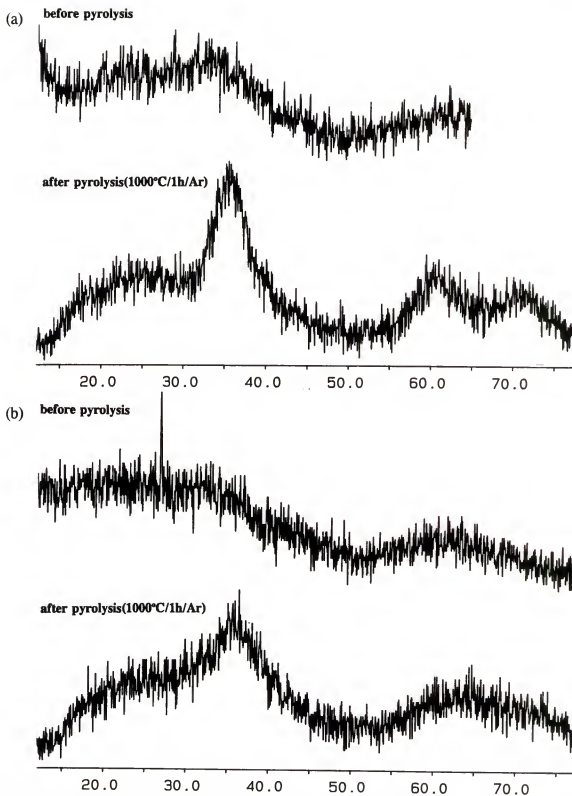


Figure 4.16 X-ray Diffraction Patterns of (a) PCS-SZ Polymer and (b) Decaborane High-dope PCS-SZ Polymer, before and after 1000°C Pyrolysis

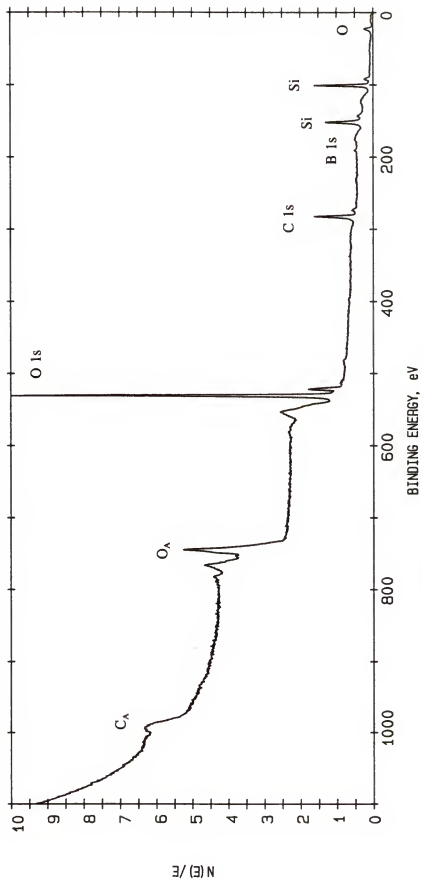


Figure 4.17 XPS Wide Scan Spectrum of Pyrolyzed Disk: Decaborane High-dope PCS-SX Polymer

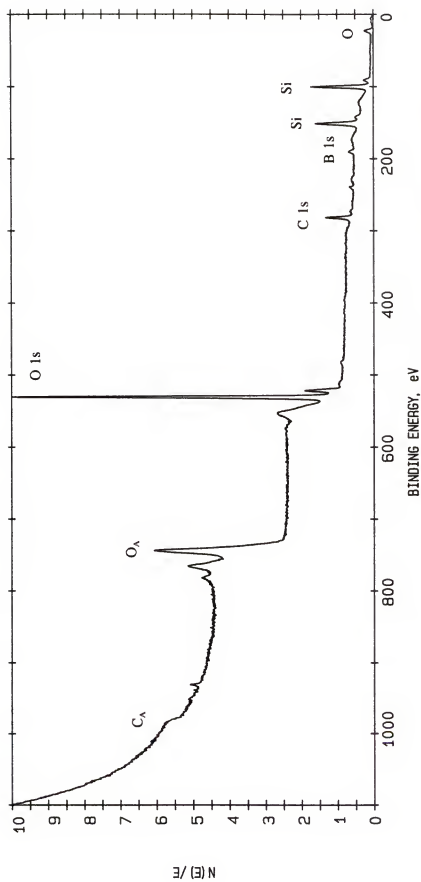


Figure 4.18 XPS Wide Scan Spectrum of Pyrolyzed Disk: Decaborane High-dope PCS-SZ Polymer

Table 4.2 Summarized XPS Results: Atomic Concentration of Pyrolyzed Disks

sample	surface	concentration (atomic %)				
		Si	C	O	B	N
PCS-SX (no DB)	as-pyrolyzed	23.4	21.5	55.2	--	--
	Ar ⁺ -sputtered	32.2	41.5	26.5	--	--
PCS-SX (15% DB)	as-pyrolyzed	23.2	18.7	55.8	2.3	--
	Ar ⁺ -sputtered	31.6	35.5	31.6	1.5	--
PCS-SZ (no DB)	as-pyrolyzed	22.3	27.6	49.1	0.9	0.1
	Ar ⁺ -sputtered	31.7	29.8	38.4	0.1	--
PCS-SZ (15% DB)	as-pyrolyzed	22.6	16.4	56.8	4.2	--
	Ar ⁺ -sputtered	26.5	12.7	54.2	6.6	--

cf. Theoretical Atomic Concentrations

component	concentration (atomic %)				
	Si	C	O	B	N
PCS-SX	20	60	20	--	--
PCS-SZ	20	60	--	--	20
SiC	50	50	--	--	--
SiO ₂	33	--	66	--	--

Boron was not detected on the surface of the pyrolyzed PCS-SX disk. Boron was measured at 2.3 and 1.5 atomic % on the as-received and sputtered surfaces of pyrolyzed PCS-SX high-dope disks, respectively. The surface of the pyrolyzed PCS-SZ disk was found to contain 0.9% boron. The PCS-SZ disks were pressed using the same mold right after the PCS-SZ high-dope disks were pressed. Since the decaborane has a strong absorption, the mold might have been contaminated to some extent with decaborane. When the PCS-SZ disks were pressed under high pressure, decaborane could be transferred from the mold surface to the disk surface. Ion sputtering removed most of the boron-contaminated surface layer. As expected, surfaces of PCS-SZ high-dope disks sustained boron contents of 4.2 to 6.6%. A strong chemical bonding between the amine in SZ and the boron in decaborane must be effective to prevent the decaborane from vaporizing during the process. Considering the heavy oxide contamination on the specimen surface, the boron content of carefully handled specimens could be very high.

Peak positions (binding energy) and full-width-at-half-maximum (FWHM) were measured from XPS narrow scan spectra. Table 4.3 summarizes those results and Table 4.4 shows XPS peak positions found in references including Perkin-Elmer Handbook. XPS peaks of hydrocarbon and gold have been used widely for the references of binding energy calibration. Theoretically, my specimens did not contain $[-CH_2-]_n$ -type hydrocarbon. A comparison of binding energies and FWHM between experimental data (Table 4.3) and reference data (Table 4.4) did not produce much information. The reasons for this were, (1) many XPS peaks for C 1s, O 1s and B 1s were broad (FWHM > 2.5 eV) in a plain parabola shape; (2) specimens were heavily contaminated by

Table 4.3 Summarized XPS Results: Binding Energy (eV) and FWHM (eV)

sample	surface	binding energy (FWHM)				
		Si	C	O	B	N
PCS-SX (no DB)	as-pyrolyzed	100.4 (1.78)	281.8 (2.13)	529.9 (1.67)	--	--
	Ar ion sputtered	98.2 (2.68)	280.9 (2.27)	529.1 (1.85)	--	--
PCS-SX (15 % DB)	as-pyrolyzed	101.0 (1.81)	282.3 (2.03)	530.6 (1.71)	191.0 (1.94)	--
	Ar ion sputtered	98.4 (2.82)	280.7 (2.29)	529.2 (1.99)	188.0 (2.78)	--
PCS-SZ (no DB)	as-pyrolyzed	100.6 (1.76)	281.7 (1.70)	530.3 (1.69)	190.6 (1.55)	--
	Ar ion sputtered	98.9 (2.80)	280.7 (2.29)	529.9 (1.67)	--	--
PCS-SZ (15 % DB)	as-pyrolyzed	101.3 (2.06)	282.7 (2.38)	530.9 (2.06)	191.3 (2.08)	--
	Ar ion sputtered	100.0 (2.73)	281.4 (2.41)	530.1 (2.17)	190.1 (3.20)	--

Table 4.4 XPS Peak Positions in Literatures

bonding	ref	C 1s	O 1s	Si 2p	B 1s
SiC	Kar91	282.4	--	100.4-100.5	--
	Tay89	282.6-283.0	--	100.3-100.7	--
	Con92	282.8	--	~ 100.8	--
graphite (C-C)	Kar91	283.6-284.2	--	--	--
	Con92	284.5	--	--	--
C-O-Si	Kar91	283.6-284.2	529.3-530.0	101.6-103.0	--
	Tay89	284.6	532.7	103.3	--
B	Con92	--	--	--	~ 187.9
BO	Con92	--	--	--	~ 193.4

cf. XPS Peak Positions in Handbook (Mui79)

element	bonding (binding energy in eV)
C 1s	MC (280.7-282.6), gr.C-C (284.2), C-O (290.2)
Si 2p	Si (98.6-100.0), SiO ₂ (103.0-103.5)
B 1s	B ₄ C (186.2), B ₁₀ H ₁₄ (187.6), BN (189.2-190.2), B ₂ O ₃ (193.1), N-BF ₃ (> 194.0)

surface oxides; and (3) there was no dependable binding energy calibration.

Fibers from PCS-based Polymers

Fibers derived from DC PCS-SZ copolymers or UF PCS-PSZ polymers without decaborane or particles are referred to as *CP* fibers. The main objective of CP fibers was to acquire reference data for the studies of CPD fibers (with decaborane), CS fibers (with Si particles) and CSD fibers (with decaborane and Si particles). Two different classes of PCS were used: DC PCS and UF PCS. PC138, PC143, PC144 and PC174-PCD156 were the studied polymers among UF PCS batches. It was found that there was a slight difference in the molecular weight distribution between UF PCS batches. DC PCS was assumed to have an uniform molecular weight because only one bottle was used in the fiber study.

CP fiber batches from DC PCS-SZ copolymers were prepared with varying compositions, i.e, SZ content and DCP content. As a preliminary experiment in the CP fiber study, DC PCS alone was processed for fibers with only DCP. Fibers spun well, but they were stuck together after 1000°C pyrolysis. Examination to see if a copolymerization between DC PCS and SZ was necessary was also conducted. SZ monomer and DC PCS were mixed without a copolymerization step and spun into fibers (CPi batch). Mixtures whose SZ content was as high as 20 w/o made good green fibers but did not make good pyrolyzed fibers.

Table 4.5 summarizes measured tensile properties of CP fibers derived from DC PCS-SZ copolymers. CP1, CP2 and CP3 fibers were prepared with PCS-SZ copolymers

Table 4.5 Tensile Properties of CP (PCS) Fibers

fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
1	12	22.0 ± 2.2	1.35 ± 0.48	114.0 ± 22.2	11.7 ± 2.6
1-13	11	19.2 ± 1.8	1.07 ± 0.38	153.8 ± 34.0	7.2 ± 3.1
2	15	34.2 ± 6.2	0.67 ± 0.50	97.7 ± 33.6	6.4 ± 4.0
3	13	26.7 ± 3.6	0.68 ± 0.46	101.5 ± 39.1	6.4 ± 2.6
1	12	19.4 ± 2.1	1.32 ± 0.40	145.7 ± 35.9	9.4 ± 2.7
1-13	10	20.0 ± 1.1	1.57 ± 0.41	121.0 ± 13.9	13.2 ± 3.8
5	12	22.3 ± 2.7	1.33 ± 0.31	114.9 ± 21.5	11.7 ± 2.8
5-12	12	20.9 ± 2.9	1.01 ± 0.57	138.6 ± 43.1	7.3 ± 2.7
5-13	12	18.9 ± 2.3	1.32 ± 0.35	174.3 ± 29.2	7.6 ± 1.5
5-14	13	20.2 ± 2.7	1.71 ± 0.64	160.1 ± 28.3	10.5 ± 2.5
5-15	12	19.0 ± 3.5	0.52 ± 0.23	202.7 ± 57.2	2.6 ± 1.2
6	13	24.4 ± 2.7	1.33 ± 0.40	133.7 ± 28.9	10.0 ± 2.3
6-14	12	22.9 ± 2.6	2.14 ± 0.92	171.8 ± 41.5	12.5 ± 3.9
6-15	11	23.5 ± 3.4	0.30 ± 0.14	169.3 ± 56.0	1.7 ± 0.5
6B	13	24.8 ± 3.0	0.97 ± 0.39	124.4 ± 27.3	7.8 ± 2.6
6B-14	11	22.4 ± 2.6	1.12 ± 0.50	138.0 ± 26.6	7.9 ± 2.9

Table 4.5 .. continued

fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
7	stuck together; not testable				
8	12	22.5 ± 2.1	0.14 ± 0.08	very low	very low
8B	13	26.4 ± 4.9	0.55 ± 0.22	129.6 ± 32.8	4.2 ± 1.3
8B-14	13	22.3 ± 3.0	0.83 ± 0.24	158.3 ± 44.3	5.3 ± 1.3
9	13	22.7 ± 2.7	1.00 ± 0.43	137.7 ± 35.3	7.2 ± 1.6
9-12	15	22.6 ± 2.8	0.89 ± 0.26	143.8 ± 30.4	6.2 ± 1.5
9-14	14	20.1 ± 2.5	1.18 ± 0.48	203.1 ± 44.1	5.7 ± 1.6
9-15	14	21.8 ± 2.2	0.45 ± 0.17	106.0 ± 18.9	4.2 ± 1.3
10	stuck together; not tested				
12	14	18.4 ± 1.8	1.07 ± 0.28	162.6 ± 28.3	6.5 ± 1.1
12-18	12	18.8 ± 2.5	0.43 ± 0.17	152.8 ± 43.1	2.7 ± 0.5
13	14	13.7 ± 0.8	2.42 ± 0.47	194.7 ± 29.0	12.5 ± 1.8
13D	15	13.5 ± 0.6	2.31 ± 0.63	204.3 ± 15.7	11.4 ± 3.0
13P	14	13.8 ± 0.5	1.86 ± 0.39	172.0 ± 16.5	10.7 ± 1.8
14	14	16.1 ± 1.3	1.75 ± 0.21	187.5 ± 27.3	9.6 ± 2.0
14N-18	13	16.0 ± 1.0	0.51 ± 0.13	174.2 ± 18.6	2.9 ± 0.6

containing 20 w/o SZ. Those fibers were pyrolyzed to make black and easily separable SiC fibers. Average fiber diameter ranged from 22 to 34 μm . Tensile strength (0.7 to 1.4 GPa) and elastic modulus (98 to 114 GPa) were not high. This may primarily be due to large diameter of fibers. Empirically it has been observed that tensile strength and elastic modulus are inversely proportional to fiber diameter.

It was thought that SZ incorporation in PCS not only helps the fiber spinning but also increases the ceramic yield of green fibers at pyrolysis. As mentioned earlier, however, the SZ content in DC PCS-SZ copolymers should be at a minimum to attain the maximum thermostability. This is attributed to two facts. One is that the SZ incorporation in crystallizable PCS molecules would increase the degree of chain branching so that it might decrease the tendency to form crystalline ceramic phases after heat-treatments. The other is that nitrogen is generally known to be more volatile than carbon. For instance, silicon nitride has a lower melting temperature ($\sim 2300^\circ\text{C}$) than silicon carbide ($\sim 2800^\circ\text{C}$). Hence, SiC fibers containing more SZ might have a lower thermostability. Nevertheless, a comparison of thermostability between different compositions would not be an easy task. This is because several factors are involved: maximum temperature of interest, duration time at the temperature, atmosphere, fatigue testing, testing temperature and so forth.

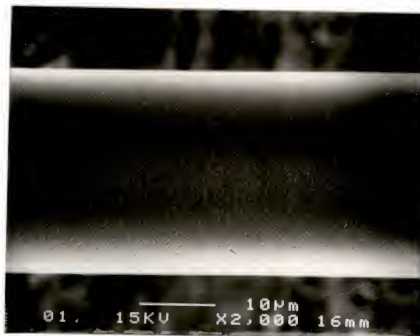
Pyrolysis or heat-treatment of fibers at elevated temperatures did not create any new crystalline phases such as Si_3N_4 , according to XRD, other than SiC. According to NAA analysis and SAM analysis of UF SiC fibers, the nitrogen content was always lower than 1 w/o. Considering that nitrogen was about 2.5 w/o in green fibers, nitrogen

must have been lost to a great extent during the pyrolysis or heat-treatments at elevated temperatures. As the preliminary experiment indicated, DC PCS cannot make good pyrolyzed SiC fibers without SZ incorporation. Therefore, the minimum SZ content is greater than zero. There would be a trade-off point (of the SZ content) which would not only provide good pyrolyzed SiC fiber but also keep the SZ content at minimum.

From CP4 batches, the minimum SZ content to give good pyrolyzed fibers was examined. SZ content was decreased from 20 w/o in CP3 to 10 w/o in CP6 fibers. Pyrolyzed CP6 fibers were in a good shape. A further decrease of SZ content to 6 w/o, as shown in CP7, CP8 and CP10 fibers, did not give pyrolyzed fibers. While CP7 and CP10 pyrolyzed fibers were all stuck, CP8 fibers were not stuck together, but quite curly overall. SEM analysis did not find a difference in surface morphology between as-pyrolyzed CP6 and CP8 fibers. An increased amount of *DCP1* (CP9) helped the fibers hold their shapes during pyrolysis. *DCP1* and *DCP2* certainly played an important role in establishing infusibility of green fibers. The minimal SZ content for DC PCS appeared to exist between 6 and 10 w/o. The compositions of CP6 fibers were used as a reference and they are referred to as *CP6 compositions*. CP12 fibers were prepared with *CP6 compositions* and were used to measure the effect of decaborane incorporation.

Figure 4.19 shows SEM surface morphology typical of as-pyrolyzed CP fibers. Compared to smooth surfaces of as-spun fibers, pyrolyzed CP fibers had some roughness of a few tenth microns in size. The surface roughness of pyrolyzed CP fibers derived from DC PCS-SZ copolymers was greater than that from UF PCS. The submicron roughness might be related to the molecular weight of polymer precursors. Considering

(a) x 2000



x 20000

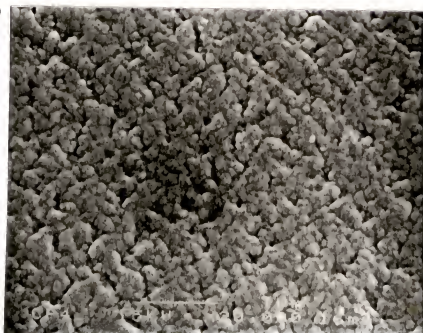
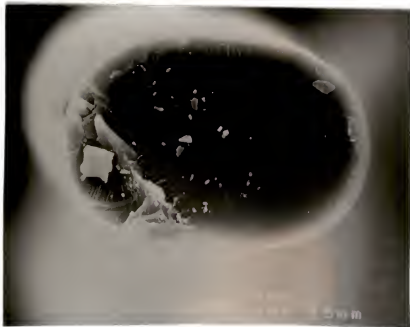


Figure 4.19 SEM Micrographs of As-pyrolyzed CP4 Fibers (DC PCS-SZ): (a) Surface and (b) Cross-section

(b) x 3500



x 20000



Figure 4.19 .. continued

that fracture is initiated from surface defects in many cases, CP fibers with a rough surface might not be expected to have good tensile strength. Cross-sections of as-pyrolyzed CP fibers had a dense microstructure. SEM work revealed that all CP fibers derived from DC PCD-SZ copolymers had elliptical cross-sections, as shown in Figure 4.20 (b) for CP4 fibers.

Average tensile strength of as-pyrolyzed CP4 to CP9 fibers was consistently around 1.3 GPa. Average elastic modulus ranged 115 to 146 GPa and rupture strain ranged 0.94 to 1.17%. The tensile strengths and the elastic moduli of those fibers, after a 1400°C heat-treatment, interestingly increased to a significant extent. The average tensile strength of CP6-14 (CP6 fiber treated at 1400°C) was 2.14 GPa compared to 1.33 GPa of as-pyrolyzed fibers. SEM micrographs of those fibers after 1400°C treatment showed smooth surfaces and rather dense cross-sections. Tensile properties of CP fibers were reduced substantially after 1500°C heat-treatment. Compared to those of CP fiber surfaces after 1400°C treatment, SEM micrographs of CP fiber surfaces after 1500°C treatment showed a porous layer on the outermost surface (about one micron thick). This surface porosity was probably responsible for the substantially reduced tensile properties of CP fibers after 1500°C treatment. CP12 fibers, a duplicate batch of CP6 fibers, did not have high as-pyrolyzed tensile strength. The overall data seems to suggest that CP fibers of decent tensile properties are not easily obtained from DC PCS-SZ copolymers.

It was expected that fibers of a lower SZ content would give a greater thermostability than those of a higher SZ content. Surfaces and cross-sections of CP4

to CP6 fibers were not noticeably different from those of CP1 to CP3 fibers. A comparison of tensile properties after heat-treatment between CP5 and CP6 fibers (CP6 has lower SZ content than CP5) did not agree with expectation. The actual results showed a slight reversed trend. The difference in strength value, however, was small.

Figure 4.20 summarizes XRD patterns of CP5 fibers with respect to the heat-treatment temperature. Pyrolyzed fibers have one broad peak near $2\theta = 35.6^\circ$. Three peaks of SiC at $2\theta = 35.6, 60.0$ and 75.5° were enlarged as fibers were treated at a higher temperature. Those three peaks corresponded to crystalline β -SiC of (111), (220) and (222) directions, respectively. The growth of those peaks resulted from the crystallization of amorphous Si-C microstructure by a thermal activation. The decrease of peak width corresponded to the grain growth of β -SiC crystals. XRD patterns of CP6 fibers after heat-treatments did not show appreciable difference from those of CP5 fibers. The effect of SZ content in DC PCS-SZ copolymers on the thermostability of resulting SiC fibers up to 1500°C was not clearly observed.

One batch of CP fibers was prepared for each UF PCS so as to obtain reference data. Properties of these fibers were to be compared with those of CPD, CS and CSD fibers. CPk and CPj fibers were produced from PC144 with PSZ (CPk) and without PSZ (CPj). CP13-series fibers and CP14 fibers were prepared from PCD156 and PC143 with 15 w/o of PSZ, respectively. The following procedure was used to prepare CP13P fibers: green CP13 fibers were cured at 400°C for an hour. Cured fibers were soaked in decaborane solution for 12 hours followed by drying in air. Dried fibers were pyrolyzed at 1000°C for an hour. CP13D fibers were obtained by soaking as-pyrolyzed

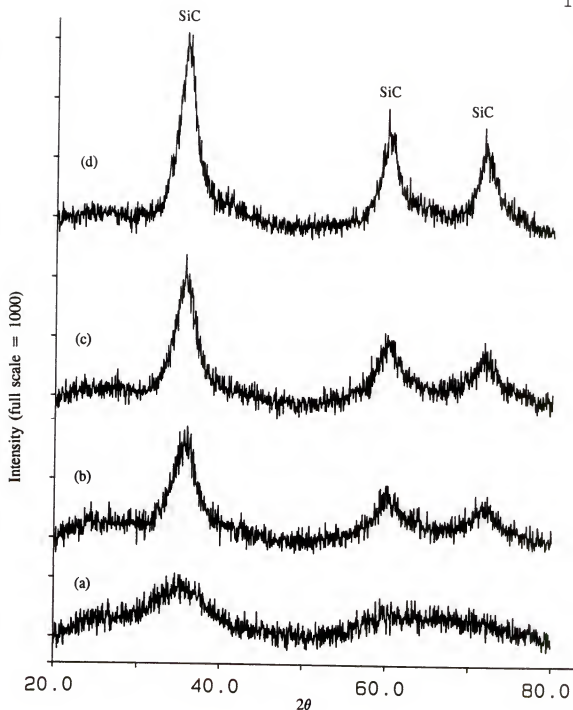


Figure 4.20 X-ray Diffraction Patterns of CP5 Fibers (DC PCS-SZ): Effect of Heat-treatment Temperature (a) after Pyrolysis, (b) after 1300°C Treatment, (c) after 1400°C Treatment and (d) after 1500°C Treatment

CP13 fibers in decaborane solution for 12 hours and by drying them. CP fibers from UF PCS have very round cross-sections. Greater ceramic yield was attained by CP fibers from UF PCS (ranging 78 to 86%) than by CP fibers from DC PCS (ranging 68 to 72%). CP13-series and CP14-series fibers were prepared for a direct comparison with some of CPD fibers. Details of those fibers will be shown in the later section.

Fibers from PCS-based Polymers with Decaborane

It was reported that an incorporation of boron compounds such as BCl_3 by CVD processing could improve the infusibility of DC PCS green fibers during pyrolysis (Lip92). Decaborane incorporation with DC PCS-SZ copolymers worked well obviously not only as a boron precursor but also as a crosslinking aid. As mentioned earlier, when decaborane is mixed with DC PCS-SZ copolymer solution, the clear mixture turned hazy in five minutes. This was most likely due to chemical reactions. When *CP6 compositions* and decaborane (CPDj) were mixed, gelation occurred during evaporation. No spinning was possible due to an excessively increased viscosity. DC PCS mixed with decaborane, with and without DCP, spun well. Pyrolyzed fibers (CPDk and CPDi, respectively) were stuck together and had low ceramic yields (62 to 69%). Therefore, when decaborane is to be incorporated in DC PCS-SZ copolymers, reasonable copolymer compositions need to be found between zero SZ content and 10 w/o SZ content.

A preliminary experiment was carried out to find the moiety with which decaborane interacts in PCS-SZ or PCS-SX copolymers. SZ or SX monomer was mixed with an equimolar amount of decaborane and left to react for several hours at room

temperature. The SZ-decaborane mixture turned hazy in five minutes. The SX-decaborane mixture stayed clear throughout. Each mixture was evaporated until it was fully solidified. It took a long time to dry up the mixture via evaporation. The evaporation of SX-decaborane solution gave a solid product whereas the SX-decaborane mixture left a product of two phases: solid and liquid. Solid phase was probably the precipitated decaborane and the liquid phase was SX. Therefore, the amine in SZ is the moiety in the copolymer that interacts with decaborane to form solid products in the solution. Weight changes of above mixtures, before and after drying, were measured. There were no noticeable weight changes by evaporation. Individual components (decaborane, SZ and SX) were dissolved in toluene and were evaporated using a rotary evaporator. SZ and SX remained as liquid while decaborane was dried to solid. Weights of those components after the evaporation were measured. No appreciable weight changes were observed in any of them. Unexpectedly, decaborane lost only a small portion of its initial weight (less than 5%) during evaporation assisted by water heating at 45°C.

CPD1 and CPD2 fibers were processed from copolymers of a reduced SZ content (PCS : SZ = 17 : 1). There were still gelation problems so that the spinning of CPD1 and CPD2 fibers was poor. Nevertheless, pyrolyzed CP1 and CP2 fibers were black and in good shape; straight and easily separable. The SZ content was reduced further in CPD3 and CPD4 batches (PCS : SZ = 45 : 1). Pyrolyzed fibers were all stuck together with low ceramic yield (61 % for CPD4). SZ content was increased a little in CPD5 and CPD6 compositions (PCS : SZ = 28 : 1). CPD5 fibers were not obtained due to over-

evaporation. CPD6 fibers spun well but partly melted during the pyrolysis. The 34 mg of decaborane was apparently not enough for that composition.

Amounts of *DCP2* and decaborane were doubled in CPD7 keeping the SZ content the same as that of CPD6. Due to a partial gelation, spinning was poor. However, pyrolyzed fibers were good. As shown by CPD8 fibers, doubling only the decaborane content of CPD6 compositions made curly fibers. Curly fibers were probably caused by a low infusibility of green fibers. Therefore, DCP also played some role in the infusibilization of green fibers. A high ceramic yield was attained for CPD7 fibers (75%). Stuck pyrolyzed fibers were always accompanied by low ceramic yields (61% and 64% for CPD4 and CPD6, respectively).

Table 4.6 summarizes measured tensile properties of CPD1 to CPD8 fibers. The variation of compositions did not show a significant effect on the tensile properties of fibers. Those fibers had intermediate tensile strengths (1.2 to 1.4 GPa) and intermediate elastic moduli (132 to 228 GPa). Tensile properties of fibers were poor after 1500°C treatment. SEM analysis revealed that CPD2-15 fibers had a very rough surface. Compared to the rupture strains of other fiber batches (over 1.2%), fibers of CPD1 to CPD8 batches have relatively low rupture strains (0.6 to 1.1%). This might be attributed to poor fiber processing due to gelation problems.

Compositions of further reduced SZ contents (PCS : SZ of CPD9 and CPD10 were 37 : 1 and 43 : 1) resulted in a better spinning as well as better tensile properties of fibers. It was thought that the reaction between SZ and decaborane may proceed further toward a better crosslinking if green fibers were aged longer. Some portions of

Table 4.6 Tensile Properties of CPD Fibers (DC PCS-SZ + decaborane): CPD1 to CPD8

fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
1	14	18.0 ± 2.6	1.23 ± 0.44	177.2 ± 53.0	7.4 ± 2.9
1-15	13	15.8 ± 2.2	0.78 ± 0.25	208.2 ± 47.3	3.7 ± 0.6
2	13	22.5 ± 3.1	1.42 ± 0.47	132.5 ± 38.4	10.7 ± 1.6
2-15	12	20.5 ± 3.2	0.51 ± 0.32	177.5 ± 59.9	2.7 ± 1.0
3	--	stuck fiber			
3	--	stuck fiber			
6	--	stuck fiber			
7	14	18.9 ± 2.2	1.31 ± 0.43	155.6 ± 32.2	8.3 ± 1.4
7-15	12	19.2 ± 2.0	0.58 ± 0.09	177.2 ± 51.5	3.4 ± 0.6
8	13	19.0 ± 2.9	1.38 ± 0.64	228.3 ± 74.5	6.0 ± 1.9
8-15	11	19.6 ± 2.0	0.38 ± 0.19	184.1 ± 46.7	2.0 ± 0.5

CPD9 and CPD10 green fibers were aged in a vacuum for 15 hours at room temperature in contrast to the normal fiber's no aging, and then pyrolyzed at 1000°C. Those aged fibers are referred to as CPD9A and CPD10A. Fibers were treated either at 1500°C or at 1800°C (or 1850°C in some cases).

Table 4.7 summarizes measured tensile properties of CPD9-series and CPD10-series fibers. No significant differences either in ceramic yield or in tensile properties of as-pyrolyzed fibers were made by the aging of green fibers. Compared to those of CP fibers from DC PCS-SZ copolymers, CPD9 and CPD10 fibers had better as-pyrolyzed tensile properties. An average tensile strength of 2.0 GPa was attained by CPD10 fibers. Interestingly, CPD9A and CPD10A fibers have better tensile strength after an 1800°C treatment than after 1500°C treatment. This was the expected principal effect of decaborane incorporation. Decaborane did not play a beneficial role for densification during a heat-treatment at 1500°C because the temperature was too low. Instead, oxidative degradation reactions might occur between residual oxygen and other elements, such as carbon and silicon:



Those reactions of gas formation would leave pores in the fibers and would decrease fiber strength to a great extent. Decaborane was active during an 1800°C treatment not only to densify the microstructure but also to enhance crystallization of SiC. Another possible factor would be the furnace type. The batch furnace for 1800°C treatment ran at a high heating rate (20°C per minute) and in a well-sealed chamber while the sealing of the tube furnace for 1500°C treatment (5.5°C per minute) relied on a rubber stopper

Table 4.7 Tensile Properties of CPD Fibers (PCS-SZ + decaborane): CPD9 to CPD11

fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
9	14	18.2 ± 1.6	1.68 ± 0.51	183.8 ± 29.6	9.1 ± 1.9
9-15	12	18.0 ± 3.4	0.86 ± 0.28	223.6 ± 59.7	3.8 ± 0.6
9A*	14	18.1 ± 1.4	1.55 ± 0.43	180.4 ± 24.7	8.6 ± 2.2
9A*-15	13	17.1 ± 1.8	0.40 ± 0.14	181.6 ± 31.6	2.2 ± 0.7
9A*-18 [#]	13	17.8 ± 2.3	1.07 ± 0.36	192.2 ± 41.0	5.5 ± 1.1
10	11	16.8 ± 2.2	1.99 ± 0.74	190.4 ± 41.1	10.6 ± 3.6
10-15	11	18.5 ± 2.1	0.44 ± 0.17	175.4 ± 36.5	2.4 ± 0.6
10A*	14	20.1 ± 2.2	1.88 ± 0.43	171.6 ± 42.3	11.5 ± 3.0
10A*-15	11	17.3 ± 2.0	0.69 ± 0.37	210.1 ± 50.9	3.1 ± 1.2
10A*-18	12	18.2 ± 1.8	1.30 ± 0.16	197.1 ± 36.2	6.7 ± 1.0
11	14	18.3 ± 2.7	1.12 ± 0.37	148.4 ± 37.3	7.6 ± 1.8
11-15	14	15.7 ± 2.6	0.72 ± 0.25	191.3 ± 56.4	3.9 ± 0.7
11-15G ^s	14	17.3 ± 2.7	0.67 ± 0.20	179.5 ± 48.0	3.8 ± 0.8
11-18	14	18.0 ± 2.6	0.74 ± 0.31	166.4 ± 52.9	4.4 ± 0.8
11B [@]	15	11.8 ± 1.0	1.50 ± 0.30	204.5 ± 39.8	7.5 ± 1.4
11B-15	13	11.7 ± 1.3	0.76 ± 0.26	215.0 ± 49.2	3.5 ± 1.0
11B-15G	15	13.6 ± 2.0	1.08 ± 0.47	215.6 ± 68.1	4.9 ± 0.9
11B-18	10	12.3 ± 1.4	0.94 ± 0.34	198.8 ± 41.5	4.7 ± 0.9

* "A" denotes 12 hour-aging of green fibers prior to pyrolysis

G "G" denotes that fibers were covered with graphite foil during 1500°C treatment.

B "B" denotes that fibers were processed by Dr. Toreki using a glove box.

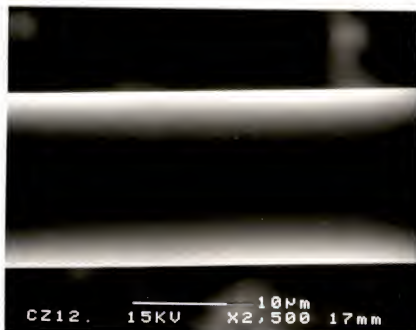
for the inert gas line.

The effect of decaborane incorporation on the fiber morphology was measured via SEM. Figure 4.21 shows SEM micrographs of CPk fiber (without decaborane), as-pyrolyzed and after an 1800°C treatment. Surfaces of CPk-18 fibers were covered with outgrown crystallites and fiber surfaces appeared porous beneath the crystallites. Tensile strength of as-pyrolyzed CPk fibers dropped to a great extent from 2.55 GPa to 0.53 GPa after 1800°C treatment. Figure 4.22 illustrates the surface morphology of CPD9A-18 and CPD10A-18 fibers. Fiber surfaces have much fewer crystallites than those of CPk-18 fibers. Fiber surfaces beneath crystallites appeared rather dense. CPD10A-18 fibers have even fewer crystallites on the surface than CPD9A-18 fibers. This fact might be related to the low SZ content of CPD10A fibers. Tensile strength retention rates of CPD9A and CPD10A fibers were rather high (69%) after the 1800°C treatment.

An attempt to find the minimum SZ content was made. The SZ content was further reduced in CPD18 compositions (PCS : SZ = 75 : 1). Fibers spun well but did not survive 1000°C pyrolysis. The ceramic yield of CPD8 (67%) was much lower than those of CPD9 and CPD10 fibers (75 and 74%). Therefore, the minimum ratio of PCS to SZ with a decaborane content of 1.5 w/o should be located between 44 : 1 to 75 : 1. With a greater decaborane content than 1.5 w/o one may be able to reduce the SZ content further.

One question raised during the fiber research was "what would be the effect of spinning under a well-controlled atmosphere during the spinning on the properties of resulting fibers?" or "Does a fiber spinning under inert gas would result in better fiber

(a)



(b)

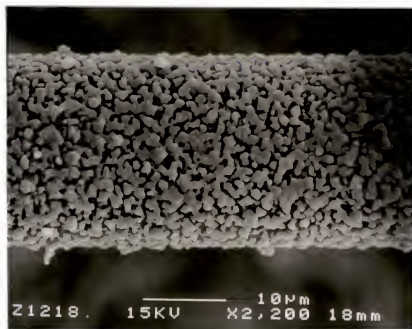
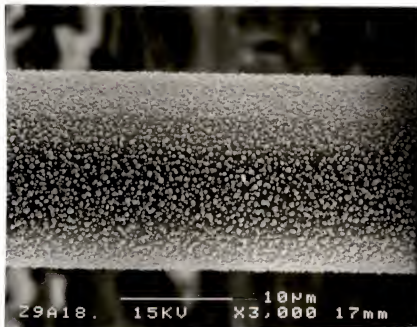


Figure 4.21 SEM Micrographs of CPk Fibers (UF PCS-PSZ): (a) As-pyrolyzed and (b) after 1800°C Treatment

(a) x 3000



x 20000

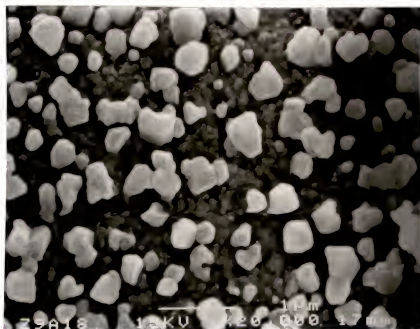
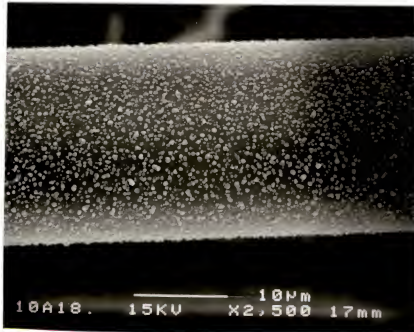


Figure 4.22 SEM Micrographs of (a) CPD9A and (b) CPD10A Fibers (DC PCS-SZ + 1.5 w/o decaborane) after 1800°C Treatment: Effect of SZ Content on Surface Morphology

(b) x 2500



x 20000

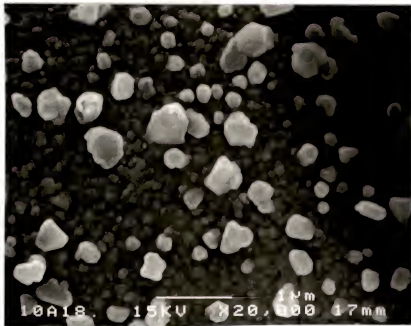


Figure 4.22 .. continued

properties?". A glove box has been used by other personnel for fiber spinning at UF. Spinning has been performed in the glove box filled with argon gas. It was attempted to process fibers from the identical polymer to evaluate the effect of spinning in a glove box on fiber properties. A copolymer mixture of CPD9 composition was reproduced. The mixture was partly evaporated and split in half. One half was given to Dr. Toreki and the other half was processed by me. Fibers spun in the glove box under argon were pyrolyzed in the Lindberg tube furnace. Fibers spun in air were pyrolyzed in the Thermolyne tube furnace. The former fibers are referred to as CPD11B while the latter fibers are referred to as CPD11. Both fiber batches were heat-treated at 1500°C or 1800°C. During one of the two separate 1500°C treatments, both fibers were covered with a graphite foil possibly to reduce the attack of residual oxygen in the furnace.

Table 4.7 summarizes measured tensile properties of CPD11 and CPD11B fibers. Fibers spun in the glove box tended to have smaller diameters (8 to 11 μm) than those spun in air (15 to 20 μm). This was probably due to the difference in the viscosity of spinning solution. Tensile properties of both CPD11 and CPD11B fibers were not good. CPD11B fibers have slightly greater tensile strength (1.5 GPa) and elastic modulus (204 GPa) than CPD11 fibers (1.1 GPa and 148 GPa). CPD11B fibers have slightly better tensile strength and elastic modulus than CPD11 fibers even after 1500°C or 1800°C treatment. However, that there was no noticeable difference in the rupture strain between those two fiber batches. Considering that smaller fibers have greater strength and elastic modulus, the slight difference in the tensile properties between these fibers seemed to originate from the difference in fiber diameter rather than in atmosphere.

Tensile strength of CPD11-18 and CPD11B-18 fibers, as consistent with CPD9A and CPD10A fibers, were greater than CPD11-15 and CPD11B-15 fibers. Tensile strength retention rates after 1800°C treatment ranged from 66 to 72%, which is similar to CPD9A and CPD10A fibers. The use of graphite foil did show significant beneficial effect on the fiber tensile properties during 1500°C treatment. SEM and XRD analysis work did not differentiate CPD11-series fibers from CPD11B-series fibers.

It has been proved that the ceramic yield of PCS increases as SZ is incorporated. A comparison of yield between CPj and CPk fibers followed this trend. Therefore, it is desirable to keep the SZ content as high as possible with decaborane incorporation for a high ceramic yield. As shown in DC PCS-SZ copolymers and in UF PCS-PSZ blends, interaction between SZ and decaborane causes problems in solution stability, i.e., gelation. It was studied if the decaborane could be deactivated by adding an amine reagent (N,N-diisopropyl-ethylamine: DPEA) for reaction with decaborane. CPD13 and CPD14 fibers were processed from *CP6 compositions* with decaborane. Table 4.8 summarizes measured tensile properties of CPD13 and CPD14 fibers. Both fiber batches did not show good as-pyrolyzed strength. As mentioned earlier, a large portion of added decaborane reacted with DPEA to form solid products. Most of the products were filtered by 0.45 μm PTFE filter so that the actual amount of decaborane left in the copolymers would be very small. SEM work indicated that CPD13-15 and CPD14-15 fibers had very rough surfaces covered with crystallites.

PC144 was used to prepare a few CPD fiber batches. It was found that UF PCS-PSZ blends of 15 w/o PSZ were gelled during evaporation when decaborane was added.

Table 4.8 Tensile Properties of CPD13 and CPD14 Fibers (DC PCS-SZ + decaborane + DPEA): Effect of Spinning Atmosphere

fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
CPD13	11	19.3 ± 3.3	0.75 ± 0.23	159.9 ± 43.5	4.7 ± 0.8
CPD13-15	13	19.5 ± 2.6	0.29 ± 0.14	177.2 ± 39.5	1.6 ± 0.4
CPD14	13	20.4 ± 2.5	1.42 ± 0.71	209.1 ± 52.1	6.5 ± 2.3
CPD14-15	14	19.0 ± 2.2	0.35 ± 0.15	190.5 ± 44.3	1.8 ± 0.5

Table 4.9 Tensile Property Comparison: Effect of Decaborane Incorporation

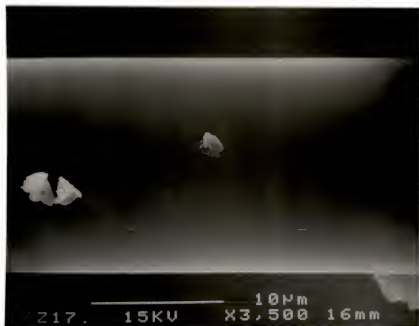
fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
CPk	11	23.3 ± 1.7	1.39 ± 0.47	137.2 ± 13.9	10.0 ± 2.6
CPk-18	13	20.4 ± 2.2	0.28 ± 0.18	141.7 ± 46.0	1.8 ± 0.8
CPj	13	14.7 ± 1.4	2.55 ± 0.61	153.7 ± 23.6	16.6 ± 3.3
CPj-15	13	15.2 ± 2.4	0.56 ± 0.17	194.8 ± 31.8	2.9 ± 0.8
CPj-18	14	19.1 ± 4.4	0.53 ± 0.20	111.8 ± 34.4	4.7 ± 0.8
CPD16-18	14	18.6 ± 3.0	0.75 ± 0.24	230.2 ± 39.7	3.3 ± 0.9
CPD17	16	17.9 ± 1.1	2.51 ± 0.65	186.7 ± 6.7	13.4 ± 3.4
CPD17-18	13	18.0 ± 1.2	1.52 ± 0.32	208.6 ± 10.5	7.2 ± 1.4

In CPD15, PSZ content was reduced to 5 w/o (PCS : PSZ = 18 : 1). The PSZ content was still too high to avoid gelation during evaporation. No fiber spinning was possible. PSZ content was reduced to 1 w/o (PCS : PSZ = 96 : 1) in CPD16 compositions. Due to a partial gelation, spinning was poor. However, pyrolyzed fibers were in good shape (straight and easily separable). Finally, no PSZ was mixed with PCS in the CPD17 batch. Decaborane and DCP2 were added to PCS. Fiber spinning was good and good pyrolyzed fibers were obtained.

Table 4.9 summarizes measured tensile properties of CPj, CPk, CPD16 and CPD17 fibers, which were all derived from PC144. As shown before, CPj fibers had average as-pyrolyzed tensile strength of 2.6 GPa, which is comparable to one of the good UF SiC fiber batches. CPD17 fibers had average as-pyrolyzed tensile strength of 2.5 GPa. Considering the strength of CPk fibers (1.4 GPa), which were prepared from PC144 without decaborane, decaborane incorporation seems to have the potential to make good pyrolyzed SiC fibers. CPD17-18 fibers had a fair average tensile strength of 1.5 GPa and elastic modulus of 209 GPa for the large diameter fibers (18 μm). Rupture strain of CPD17-18 fibers was much larger (over 0.7 %) than any SiC fibers prepared without decaborane after 1800°C treatment. Due to the small amount of fibers, as-pyrolyzed CPD16 fibers were not tested for tensile properties. Properties of CPD16-18 seemed to stand in-between CPj-18 and CPD17-18 fibers, as expected from the in-between compositions.

Figure 4.23 illustrates the surface morphology of CPD17 fibers, as-pyrolyzed and after an 1800°C treatment. No crystallites were seen on the surface of CPD17-18 fibers.

(a)



(b)

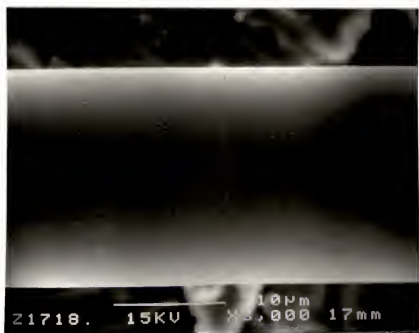


Figure 4.23 SEM Micrographs of CPD17 Fibers (UF PCS + 3.2 w/o decaborane); (a) As-pyrolyzed and (b) after 1800°C Treatment

Compared to very smooth surfaces of CPD17 fibers, CPD17-18 fibers have slight surface roughness (shallow valleys), where crack initiation might have occurred for the fracture at reduced strength. Table 4.10 summarizes tensile properties of SiC fibers patented recently by Dow Corning (Lip91). Three different gas precursors were employed by Dow for the boron incorporation: (A) $\text{BCl}_3 + \text{NH}_3$, (B) $\text{NO} + \text{B}_2\text{H}_6$ and (C) $\text{NO} + \text{BCl}_3$. Processing temperatures and time are summarized in the table. DC SiC fibers have relatively low as-pyrolyzed tensile strength (1.5 to 1.9 GPa) but retain the strength at a high level (66 to 110%) after 1800°C treatment. They also have a high elastic modulus (177 to 270 GPa) after 1800°C treatment. Nicalon SiC fibers of a ceramic grade were heat-treated and tested together for a direct comparison. It was reported that Nicalon fibers were too weak after 1800°C treatment to be tested for tensile properties.

There are several factors to take into account when DC SiC fibers and CPD17 fibers are compared. The first one is the fiber size. Average diameters of DC SiC fibers (7 to 8 μm) are much smaller than CPD17 fibers (18 μm). In the sense of fiber volume, CPD17 fibers are four times larger than DC SiC fibers. Considering the inverse relation between fiber diameter and tensile properties, CPD17 fibers seems to have a greater potential for tensile properties than DC fibers. A second factor concerns the processing. Boron incorporated CPD fibers requires only a simple additional processing: mixing of PCS solution with decaborane. Otherwise, CPD fibers are processed in the same way as other UF SiC fibers are. On the other hand, as shown in Table 4.10, a time and energy-consuming CVD process was needed for DC SiC fibers. The last point concerns the shape of products. It was reported that DC SiC fibers were produced in

Table 4.10 Summarized Properties of Dow Corning New SiC Fibers

fiber batch name	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	crystallite size ($\text{\AA}$)
A*-1200	7.7 ± 0.5	1.48 ± 0.34	172.4 ± 21.4	~ 550
A-1800	6.8 ± 0.2	1.63 ± 0.50	220.7 ± 16.6	
Nic-1800	--	not testable	--	
B*-1200	7.4 ± 0.2	1.70 ± 0.32	191.0 ± 9.0	
B-1800	6.9 ± 0.1	1.13 ± 0.32	177.2 ± 9.0	
Nic-1800	--	not testable	--	
C*-1200	8.8 ± 0.3	1.87 ± 0.43	178.6 ± 13.1	
C-1800	7.8 ± 0.2	1.68 ± 0.13	269.7 ± 11.0	
Nic-1800	--	not testable	--	

* A: $\text{BCl}_3 + \text{NH}_3$ (BCl_3 30% in Ar: 25-140°C for 4 hr, NH_3 13% in Ar for 15 hr)

B: NO + diborane (NO 33% in Ar: 25-200°C > 24 hr, diborane)

C: NO + BCl_3 (NO 33% in Ar: 25-200°C > 24 hr, BCl_3 30% in Ar: 25-140°C > 4 hr)

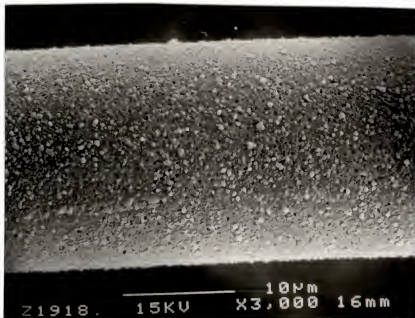
non-continuous form while CPD17 fibers were continuous fibers on a batch scale. As will be shown later, the fiber property improvement via decaborane incorporation is very reproducible. Considering those factors, the decaborane approach appears to have a great potential to produce SiC fibers of good thermomechanical stability up to 1800°C.

It was speculated that the tiny roughness on CPD17-18 fiber surfaces might be attributed to the low decaborane content. CPD19, CPD20 and CPD21 fibers were prepared varying the decaborane content. CPD21 was the duplicate of CPD20 because the latter fibers were spun poorly. The decaborane content of CPD17 fibers was 3.2 w/o while that of CPD19 and CPD 21 fiber were 1.1 and 7.6 w/o, respectively. Table 4.11 summarizes measured tensile properties of CPD17, CPD19 and CPD21 fibers. CPD19 fibers had good as-pyrolyzed tensile strength (2.2 GPa), but have poor strength (0.7 GPa) after 1800°C treatment. CPD21 fibers had rather low as-pyrolyzed strength (1.9 GPa), but have decent strength (1.4 GPa) after 1800°C treatment. Figure 4.24 shows the SEM micrographs of the surfaces of CPD19-18 and CPD21-18 fibers. CPD19-18 fibers had rough surfaces with crystallites and a large number of pores. CPD21-18 fibers had a surface as smooth as that of CPD17-18 fibers. No difference was observed in the SEM micrographs of cross-sections between CPD17-18, CPD19-18 and CPD21-18 fibers. The results suggest that there was a certain level of decaborane required for a good surface densification. Above that level, an increase of decaborane content did not work as efficiently. Confirming and optimization experiments are clearly needed.

Table 4.11 Tensile Property Comparison: Effect of Decaborane Content

fiber batch name	DB conc. (w/o)	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
CPD19	1.1	14	19.0 ± 0.9	2.16 ± 0.41	181.5 ± 7.5	11.9 ± 2.3
CPD19-18		13	19.0 ± 0.5	0.68 ± 0.22	210.6 ± 19.8	3.2 ± 0.8
CPD17	3.2	16	17.9 ± 1.1	2.51 ± 0.65	186.7 ± 6.7	13.4 ± 3.4
CPD17-18		13	18.0 ± 1.2	1.52 ± 0.32	208.6 ± 10.5	7.2 ± 1.4
CPD20	7.6	13	24.4 ± 4.0	1.43 ± 0.57	153.4 ± 44.6	9.2 ± 2.1
CPD21	7.6	16	17.3 ± 0.6	1.90 ± 0.41	206.9 ± 8.5	9.1 ± 1.8
CPD21-18		15	16.7 ± 0.7	1.39 ± 0.22	211.9 ± 13.9	6.6 ± 1.2

(a)



(b)

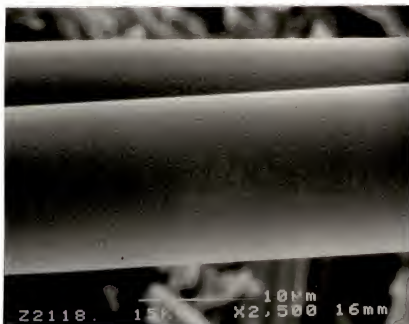
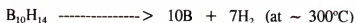
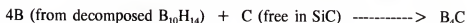


Figure 4.24 SEM Micrographs of (a) CPD19 (1.1 w/o decaborane) and (b) CPD20 Fibers (7.5 w/o decaborane) after 1800°C Treatment: Effect of Decaborane Content on Surface Morphology

Most CP and CPD fibers, after 1800°C treatment, have surfaces with more or less roughness while their cross-sections are rather dense. CP12-18 fibers have a micron thick porous layer at the outermost surface. This fact suggests that the fiber surface is the region which requires a good densification. According to previous TG/DTA analysis of decaborane, it may vaporize to a great extent from the green fibers during the slow heating to 150°C before a heating to 1000°C for pyrolysis leaving a surface depleted zone. A reference (Mer89) suggests a decomposition reaction of decaborane as follows:



If there is free carbon is present when the decomposition reaction occurs, there should be a greater chance for the following reaction to take place and produce boron carbides:



Decaborane needs to stay on the fiber surface until a reaction occurs to convert it to ceramic during pyrolysis. Two approaches to provide the fiber surface with increased decaborane content were studied; soaking of fibers in decaborane solution and in decaborane-SZ complex solution. CP13 and CP14 fibers were prepared and studied for the effect of soaking in decaborane-based solutions. Those fibers were produced from PCD156 and PC143 with PSZ (15 w/o) and without decaborane. CPD23F and CPD24F fibers were prepared from PCD156 with decaborane (3.1 and 3.2 w/o). *F* denotes *fast pyrolysis* and will be discussed later. CPD24FD fibers were obtained by soaking CPD24F fibers in decaborane solution and drying them. *D* after the batch number denotes *soaking in decaborane solution for 12 hours*. Table 4.12 summarizes measured tensile properties of CP13-series and CPD23F and CPD24F-series fibers. CP13

Table 4.12 Tensile Property Comparison: Effect of Soaking in Decaborane Solution

fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
CP13	14	13.7 ± 0.8	2.42 ± 0.47	194.7 ± 29.0	12.5 ± 1.8
CP13-18	--				
CP13D	15	13.5 ± 0.6	2.31 ± 0.63	204.3 ± 15.7	11.4 ± 3.0
CP13D-18	--				
CP13P	14	13.8 ± 0.5	1.86 ± 0.39	172.0 ± 16.5	10.7 ± 1.8
CP13-18	--				
CPD23F	13	15.4 ± 2.9	2.13 ± 0.86	197.8 ± 44.7	10.7 ± 3.2
CPD23F-18	14	14.4 ± 1.7	1.51 ± 0.38	257.1 ± 62.3	5.9 ± 0.9
CPD24F	13	13.3 ± 1.3	2.27 ± 0.59	191.1 ± 9.3	11.9 ± 3.0
CPD24F-18	16	12.3 ± 0.5	1.42 ± 0.30	251.8 ± 16.4	5.7 ± 1.2
CPD24FD18	15	13.3 ± 1.0	0.82 ± 0.34	258.8 ± 22.0	3.1 ± 1.1
CP14	14	16.1 ± 1.3	1.75 ± 0.21	187.5 ± 27.3	9.6 ± 2.0
CP14-18	--				
CP14M-18	--				
CP14N-18	13	16.0 ± 1.0	0.51 ± 0.13	174.2 ± 18.6	2.9 ± 0.6
CPD22	15	14.7 ± 1.4	2.48 ± 0.92	192.1 ± 12.8	12.7 ± 4.1
CPD22-18	14	13.6 ± 0.5	1.79 ± 0.28	242.4 ± 21.4	7.4 ± 0.9

D: soaking in decaborane solution for 12 hours

M: soaking in decaborane-SZ monomer solution for 12 hours

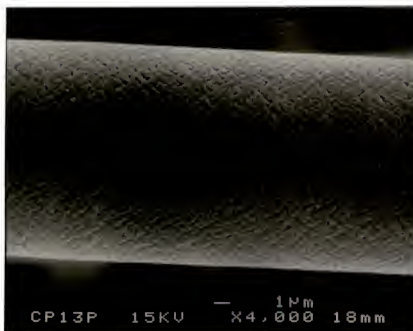
N: soaking in decaborane-PSZ solution for 12 hours

and CP13D fibers have decent as-pyrolyzed tensile strength (2.4 and 2.3 GPa). CP13P fibers have a little less strength (1.9 GPa). CP13-18, CP13D-18 and CP13P-18 fibers might be testable, but were not tested for tensile properties. Those fibers were very fragile and stuck together. Their tensile properties would be extremely low. Figure 4.25 shows SEM micrographs of surfaces of CP13P, CP13P-18, CP13-18 and CP13D-18 fibers. As-pyrolyzed CP13P fibers had a surface of typical CP fibers. However, after 1800°C treatment, the fiber surface became rough and porous. Surface of CP13-18 fibers has fewer crystallites and less roughness than that of CP13D-18 fibers.

CPD24FD fibers were obtained by soaking CPD24F fibers in decaborane solution for 12 hours and drying them. Table 4.12 summarizes measured tensile properties of CPD23F and CPD24F-series fibers. CPD23F-18 and CPD24F-18 fibers had typical strength retention rates (71 and 63%) of CPD fibers. CPD24FD-18 fibers had low strength (0.8 GPa) similar to CP13D-18 fibers. Figure 4.26 illustrates SEM surface morphology of CPD23F-18 fibers. Some fibers had a very smooth surface while others had a rough surface. Figure 4.27 shows SEM micrographs of surfaces of CPD24F-18 and CPD24FD-18 fibers. Surfaces of CPD24F-18 fibers appeared similar to that of the rough CPD23-18 fibers. The surface of CPD24FD-18 fibers was rough even though a good densification was observed. Fiber surfaces had surface grains (up to one micron).

Figure 4.28 summarizes XRD patterns of CP13-series and CPD24F-series fibers after 1800°C treatment. CPD24F-18 fibers had much larger peaks than CP13-18 fibers. Those four peaks correspond to crystalline β -SiC. Therefore, decaborane appeared to enhance the crystallization process of β -SiC. This trend was confirmed by comparisons

(a)



(b)

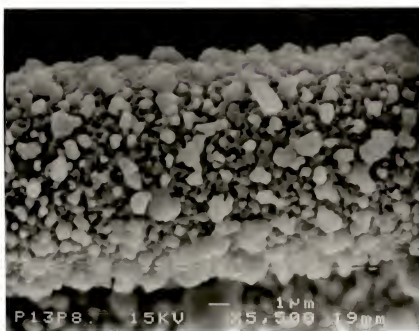
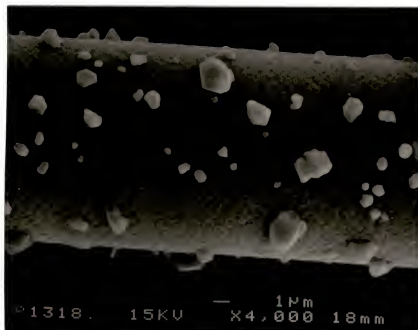


Figure 4.25 SEM Micrographs of (a) CP13P Fibers (UF PCS), (b) CP13P after 1800°C Treatment, (c) CP13 after 1800°C Treatment and (d) CP13D Fibers (soaked in decaborane solution) after 1800°C Treatment

(c)



(d)

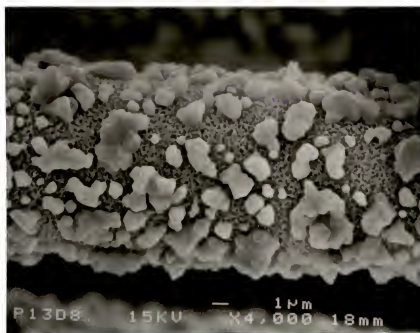
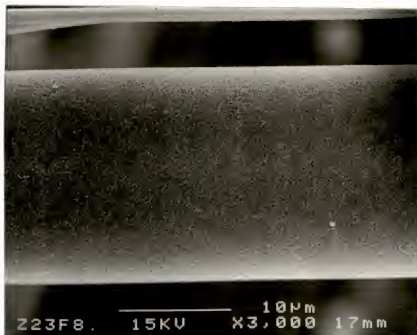


Figure 4.25 .. continued

(a)



(b)

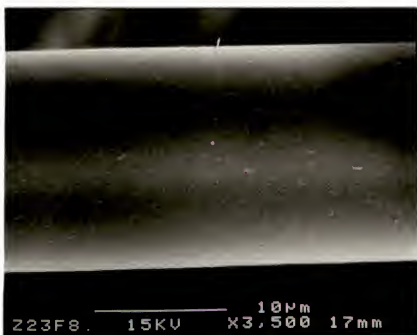
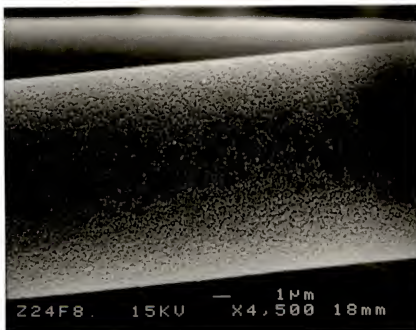


Figure 4.26 SEM Micrographs of CPD23F Fibers (3.1 w/o decaborane: fast heating):
(a) Rough Surface and (b) Smooth Surface after 1800°C Treatment

(a)



(b)

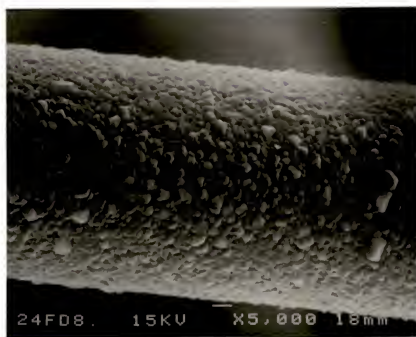


Figure 4.27 SEM Micrographs of (a) CPD24F (3.2 w/o decaborane) and (b) CPD24FD Fibers (soaked in decaborane solution) after 1800°C Treatment: Effect of Soaking in Decaborane Solution on Surface Morphology

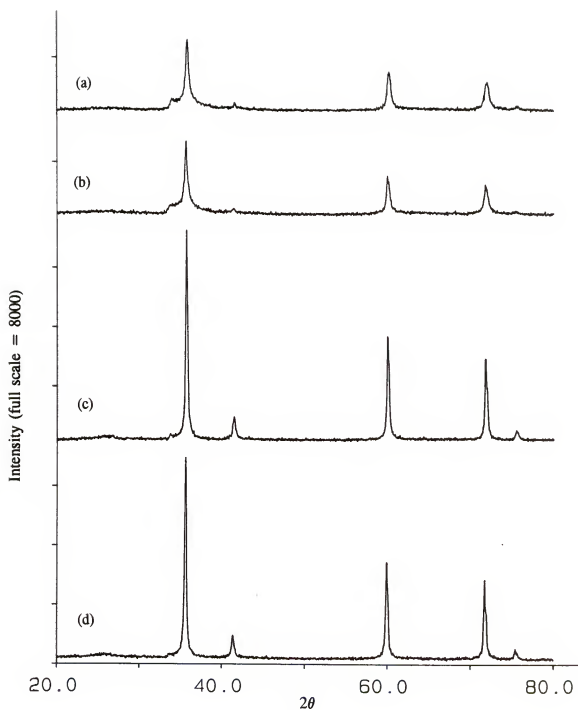


Figure 4.28 X-ray Diffraction Patterns of CP13-18 and CPD24F Fibers: Effect of Soaking in Decaborane Solution after 1800°C Treatment (a) CP13, (b) CP13 with Soaking, (c) CPD24F and (d) CPD24F Fibers with Soaking

of XRD patterns between other CP fibers (CP9 and CP12) and CPD fibers. Additionally, decaborane seemed to suppress the transformation of β -SiC to α -SiC during 1800°C treatment. α -SiC is a thermodynamically favored form of crystalline SiC at temperatures over 1600°C. The formation of α -SiC is represented by a shoulder peak at $2\theta = 34.2^\circ$. Comparisons of XRD patterns between CP13-18 and CP13D-18 fibers and between CPD24F-18 and CPD24FD-18 fibers suggested that decaborane soaking tends to slightly restrain the grain growth and slightly enhance the crystallization of β -SiC. The overall results imply that soaking of pyrolyzed fibers or green fibers in decaborane solution for 12 hours did not help boron-aided surface densification much.

Decaborane soaking did not work effectively for the surface densification probably due to the volatility of decaborane. We studied if soaking of pyrolyzed fibers in the decaborane-SZ mixture solution could be more effective. CP14M and CP14N fibers were obtained by soaking CP14 fibers in decaborane-SZ solution in toluene and decaborane-PSZ solution, respectively, for 12 hours and drying them. CPD22 fibers were made from PC143 with decaborane (3.4 w/o). Table 4.12 summarizes measured tensile properties of CP14-series and CPD22 fibers. CP14 fibers did not give good as-pyrolyzed tensile strength (1.8 GPa) while CPD22 fibers had decent as-pyrolyzed tensile strength (2.5 GPa). CP14-18 and CP14M-18 fibers were so fragile and heavily stuck together that tensile testing was not performed. CP14N-18 fibers had a slightly better shape than CP14M-18 fibers, but their tensile strength was not high (0.51 GPa). On the other hand, CPD22-18 fibers had excellent tensile strength (1.8 GPa) and a decent strength retention (72%).

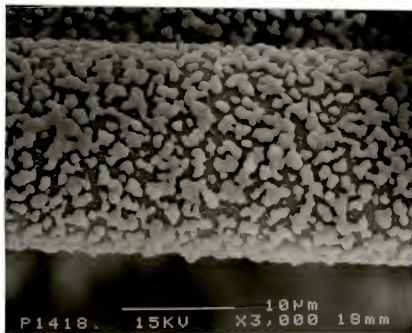
Figure 4.29 shows SEM micrographs of surfaces of CP14-18, CP14N-18 and CP14M-18 as well as a cross-section of CP14M-18 fibers. CP14-18 fibers had a typical surface of CP fibers after 1800°C treatment: a rough surface background covered with crystallites. CP14N-18 fibers had a rather clean surface, comparable to good CPD fibers after 1800°C treatment. The surface of CP14M-18 fibers was slightly rougher than that of CP14N-18 fibers. As shown in Figure 4.29(d), however, some CP14M-18 fibers were bonded together, and this is what made a separation of individual fibers very difficult. A simple explanation for this phenomenon would be that fibers were in intimate contact with others when they were pyrolyzed or heat-treated. Compared to decaborane alone, decaborane-SZ complex absorbed on fiber surfaces was less volatile so that it did not vaporize much until being converted to boron compounds. When the treatment temperature was as high as 1800°C, surface-residing boron compounds act as sintering aids to bond fibers. Bonded fibers were not observed among CP or CPD fibers after 1800°C treatment. This suggests that the surface boron level of CPD fibers was not high enough to cause fiber bonding.

Table 4.13 summarizes XRD results for several CP and CPD fiber batches to show the effect of decaborane incorporation on the fiber crystallinity. Crystallite size of fibers were calculated from XRD peak data using Scherrer approximate formula:

$$t = \frac{0.9\lambda}{B\cos\theta_B}$$

where t = crystallite size, λ = wavelength of x-ray (1.5406 Å for Cu K α), B = FWHM of the peak and θ_B = Bragg angle. Peaks for SiC(111) at $2\theta = 35.6^\circ$ were used for the

(a)



(b)

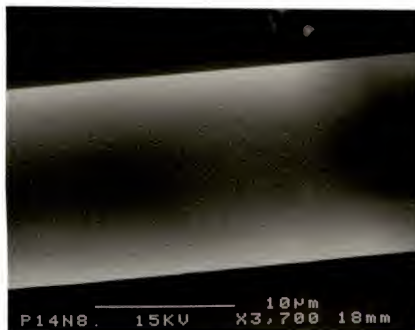
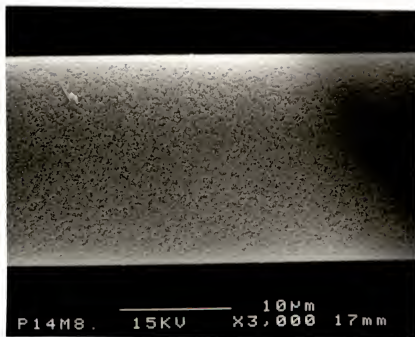


Figure 4.29 SEM Micrographs of Surfaces of (a) CP14 (UF PCS), (b) CP14N (soaked in decaborane-SZ solution), (c) CP14M (soaked in decaborane-PSZ solution) and Cross-section of (d) CP14M Fibers after 1800°C Treatment

(c)



(d)



Figure 4.29 .. continued

Table 4.13 Summarized XRD Results: Effect of Decaborane Incorporation on Crystallinity after 1800°C Treatment

decaborane incorporated?	PCS	batch name	crystallite size (Å)	peak area (deg·count)
no	DC PCS	CP9	197	430
	F4 PCS	CPj	208	443
	FD PCS	CP13	223	345
yes	DC PCS	CPD9A	263	688
		CPD10A	278	871
	F4 PCS	CPD17	292	839
	FD PCS	CPD24F	309	727

calculation. The amount of crystalline phase corresponds to the area below each XRD peak. Peak areas were calculated using the following equation and used to compare the crystallinity of fibers on a relative basis:

$$\text{peak area } (^{\circ} \cdot \text{count}) = \frac{1}{2} \text{ FWHM } (^{\circ}) \cdot \text{peak height (count)}$$

Peaks at $2\theta = 35.6^{\circ}$ for SiC (111) of CPD fibers tended to become sharper (greater in height and narrower in width) than those of CP fiber after 1800°C treatment. According to two above equations, CPD fibers have not only more crystallites but also larger grain size than CP fibers after 1800°C treatment. Since decaborane was initially expected to play some role in restricting grain growth as well as in densification, the indication was a little surprising. It was observed that crystallinity of fibers is proportional to their crystallite size. Figure 4.30 shows a plot of the crystallinity of CP and CPD fiber batches versus their crystallite size. Average elastic modulus of those fiber batches is plotted versus crystallite size in Figure 4.31. Decaborane incorporation helped SiC fibers not only to have more crystallinity after 1800°C treatment but also to have a greater elastic modulus. However, it is not clearly understood how a smaller peak width was produced by decaborane incorporation. The crystallite size needs to be measured via TEM analysis. Crystallite size of all CPD fibers (250 to $300 \text{ \AA}$) was smaller than that of DC SiC fibers ($\sim 500 \text{ \AA}$).

Density of fibers was measured by the sink-float method. Table 4.14 summarizes the measured density of selected CP and CPD fibers, as-pyrolyzed and after 1800°C treatments. Two density measurements by weight change and by pycnometer gave very close density values. Density of as-pyrolyzed CP and CPD fibers was in a narrow range

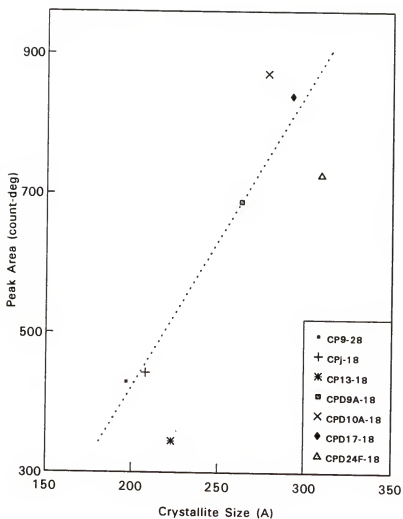


Figure 4.30 Plot of XRD Peak Area versus Crystallite Size: CP (PCS) and CPD (PCS + decaborane) Fiber Batches after 1800°C Treatment

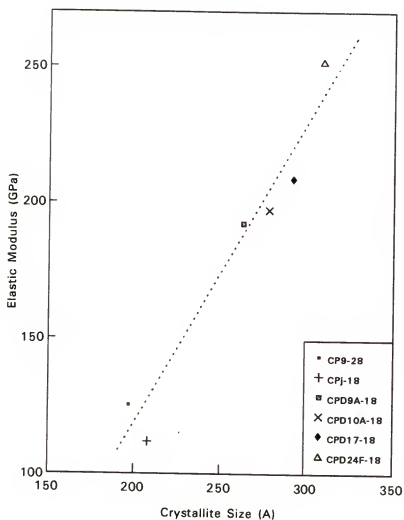


Figure 4.31 Plot of Elastic Modulus versus Crystallite Size: CP (PCS) and CPD (PCS + decaborane) Fiber Batches after 1800°C Treatment

Table 4.14 Measured Density of SiC Fibers after Pyrolysis and 1800°C Treatment:
Effect of Decaborane Incorporation

fiber batch	fiber density (g/cm ³)	
	weight measurement	pycnometer
CPj	2.463	NA
CPj-18	2.639	NA
CPD16	2.424	2.418
CPD16-18	2.792	2.785
CPD17	2.452	NA
CPD17-18	2.833	2.837
CPD10A	2.508	NA
CPD10A-18	2.641	NA
CSD17	2.367	NA
CSD17-18	2.919	2.913

(2.42 to 2.51 g/cm³). The density of CPD17 fibers increased to 2.83 after an 1800°C treatment while that of fibers with rough surfaces such as CPj-18 and CPD10A-18 increased slightly to 2.64. CPD16 fibers, prepared from the compositions in-between CPj and CPD17 fibers, have a density in-between the above values.

Fibers from PCS-based Polymers with Si Particles

Results from carbide reaction study suggested that Si particles added to PCS-based polymers could create additional SiC crystalline phase by consuming unwanted excess carbon at temperatures under 1400°C. Fibers derived from Si particle filled polymers are referred to as CS fibers. Si incorporation was expected not only to improve the stoichiometry but also to increase the thermostability of fibers. Two classes of PCS were studied: DC PCS and UF PCS (PC138).

As mentioned earlier, use of smaller Si particles is desirable for better reaction conversion and better homogeneity. Si particles acquired from another research lab were aged for several years. They might have been aggregated severely. Figure 4.32 illustrates the size distributions of as-received Si particles and fractionated Si particles. The median diameter of as-received Si particles was 0.92 μm . Fractionation of Si particles was performed as described in the experimental section. The median diameter of fractionated Si particles was about 0.15 μm . Particles as large as 0.6 μm were contained in the fractionated Si solution. Measurements of particle sizes of other fractionated Si solutions gave similar results. The fractionated Si solutions had a solid content of approximately 0.3 w/o. Therefore, the recovery rate of Si particles by a

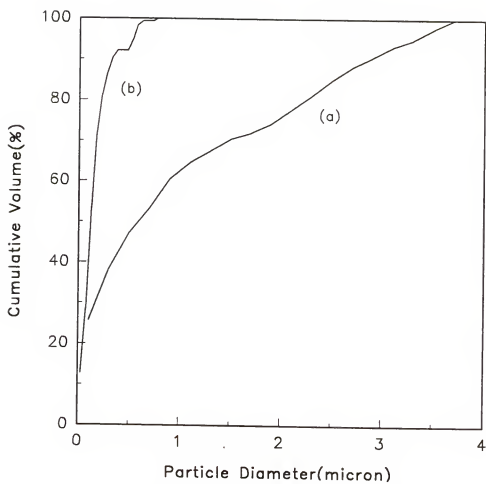


Figure 4.32 Particle Size Distribution of (a)As-received and (b)Fractionated Si Particles

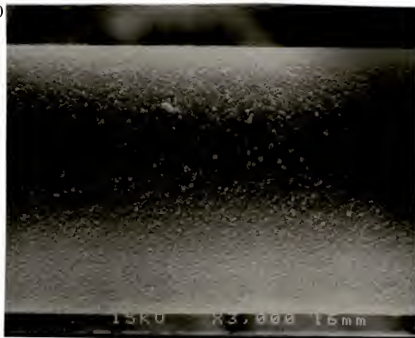
fractionation was about 1%. The remaining part of the settling solution was re-fractionated. However, the solid content of the re-fractionated Si solution dropped to 0.2 w/o. For consistent results, Si particle solutions from a re-fractionation were not used.

Two loadings of Si particles were considered: 14 and 25 w/o. Even though the copolymer-Si mixtures were prepared by accurate weight measurements, the actual Si content of each batch of green fibers was not certain. The mixture was a very viscous fluid when it was ready for spinning. Therefore, there was always a significant loss when the viscous mixture was transferred from a flask to spinneret. Si particles may stick to flask wall in a different manner from that of polymers, which would slightly change the content of incorporated Si particles.

Si particles incorporated in CS1 fibers were fractionated in aqueous solution and then were suspended in toluene. Pyrolyzed CS1 fibers were curly, metallic shiny fibers. Tensile properties of CS1 fibers were too poor to be listed in the table. Si particles from CS2 fiber batches were in toluene. CS2 green fibers were examined with SEM to see if Si particles were uniformly distributed. It was found that Si particles were well distributed and most particles were less than 0.2 μm . Figure 4.33 shows SEM micrographs of surface and cross-section of typical as-pyrolyzed CS fibers. Fibers had Si particles of a few tenths of microns well distributed on the surface. Cross-sections were dense and contained well distributed Si particles.

Table 4.15 summarizes measured tensile properties of CS fibers derived from DC PCS-SZ copolymers. CS2 and CS3 fibers had good as-pyrolyzed tensile strength (1.4 to 1.5 GPa) and elastic modulus (136 to 149 GPa) for 25 μm -diameter fibers. CS4, CS6

(a) x 3000



x 20000

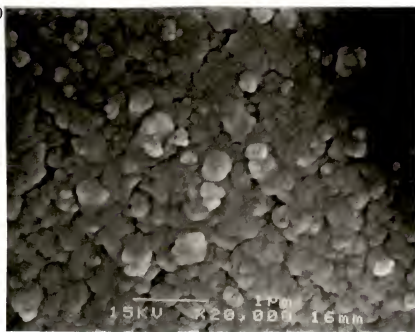
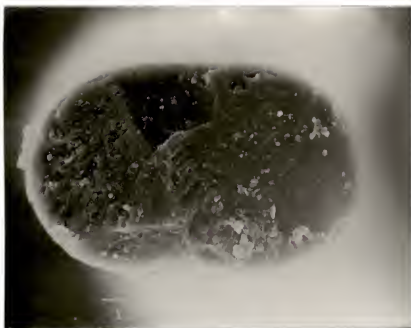


Figure 4.33 SEM Micrographs of As-pyrolyzed CS5 Fibers (DC PCS-SZ + 14 w/o Si):
(a) Surface and (b) Cross-section

(b) x 3500



x 20000

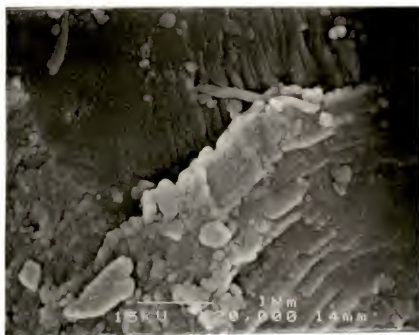


Figure 4.33 .. continued

Table 4.15 Tensile Properties of CS Fibers (DC PCS-SZ + Si) : CS2 to CS11

fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
2	9	25.7 ± 2.6	1.36 ± 0.47	149.1 ± 30.2	9.0 ± 2.4
3	9	25.1 ± 2.3	1.49 ± 0.26	135.6 ± 24.3	11.0 ± 0.9
3-13	11	24.9 ± 2.9	1.23 ± 0.56	139.0 ± 44.5	8.7 ± 2.5
3-14	10	22.8 ± 4.0	0.37 ± 0.13	137.6 ± 36.5	2.7 ± 0.8
3-15	10	25.1 ± 3.0	0.32 ± 0.14	138.7 ± 27.2	2.3 ± 0.9
4	11	16.0 ± 1.2	1.35 ± 0.35	137.3 ± 22.0	9.8 ± 1.7
4-14	12	14.2 ± 1.7	0.43 ± 0.21	119.2 ± 23.6	3.5 ± 1.5
5	13	34.8 ± 6.1	1.15 ± 0.25	100.1 ± 16.4	11.6 ± 1.7
6	11	16.5 ± 2.2	1.54 ± 0.25	164.0 ± 27.4	9.6 ± 1.7
6-S14	10	17.6 ± 1.8	1.03 ± 0.13	155.5 ± 25.9	6.7 ± 0.5
6-14	9	17.9 ± 2.3	1.12 ± 0.21	143.8 ± 15.5	7.9 ± 1.8
6B	11	19.4 ± 2.0	1.21 ± 0.33	126.6 ± 17.2	9.4 ± 1.8
6B-14	12	25.9 ± 5.7	0.39 ± 0.24	105.3 ± 28.6	3.5 ± 1.4
7	10	35.3 ± 2.9	0.83 ± 0.24	85.3 ± 8.9	9.8 ± 3.1
7-12	11	36.4 ± 4.7	0.67 ± 0.29	109.6 ± 29.9	6.0 ± 1.6
7-15	9	31.2 ± 2.5	0.59 ± 0.17	106.2 ± 17.3	5.6 ± 1.8

Table 4.15 .. continued

fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
8	11	16.8 ± 2.2	1.56 ± 0.38	136.5 ± 26.4	11.5 ± 1.7
8-14	10	14.6 ± 3.0	1.35 ± 0.59	177.9 ± 50.0	7.6 ± 2.2
8B	10	26.1 ± 2.8	0.87 ± 0.24	108.2 ± 19.9	8.2 ± 2.8
8B-14	11	24.3 ± 3.1	0.95 ± 0.52	114.7 ± 32.5	7.9 ± 2.8
9	12	16.9 ± 3.5	1.15 ± 0.37	138.1 ± 29.4	8.3 ± 1.7
9-13	11	19.3 ± 2.3	1.26 ± 0.33	186.0 ± 39.1	6.7 ± 0.9
9-14	12	18.5 ± 2.4	1.45 ± 0.27	178.5 ± 37.5	8.2 ± 0.7
9-15	13	17.2 ± 3.1	0.49 ± 0.21	195.5 ± 53.2	2.5 ± 0.6
10	Heavily stuck together: Not testable				
11	14	19.4 ± 3.6	1.00 ± 0.43	138.5 ± 41.7	7.5 ± 3.0
11-12	13	15.9 ± 2.4	1.24 ± 0.48	244.7 ± 65.4	5.0 ± 1.0
11-13	10	16.8 ± 3.1	0.78 ± 0.45	227.6 ± 65.8	3.3 ± 1.4
11-15	7	16.3 ± 3.4	0.89 ± 0.34	217.6 ± 36.9	4.1 ± 1.4
11-18	11	14.4 ± 1.5	0.23 ± 0.14	219.5 ± 53.9	1.0 ± 0.5

and CS8 fibers, even with a smaller average diameter, had a tensile strength and elastic modulus similar to those of CS2 and CS3 fibers. CS9 and CS11 fibers were prepared with reduced SZ content. Tensile strength of those fibers was slightly poorer than that of CS fibers with a higher SZ content. Figure 4.34 shows the effect of Si particle incorporation on tensile properties. Average tensile strength and average elastic modulus of each CP and CS fiber batch were plotted with respect to average fiber diameter. No positive or negative effect of Si incorporation on tensile properties was observed. It might be concluded that either 14 w/o of Si was not high enough to make difference in fiber properties or that the Si particles themselves had tensile properties similar to those of the polymer-derived SiC structure.

Figure 4.35 illustrates XRD pattern for CS9 fibers as treatment temperature increased. As-pyrolyzed fibers had three large peaks for Si particles and one broad shoulder for SiC. Compared to that of green CS fibers, the intensity of Si peak at $2\theta = 28.5^\circ$ did not change after 1000°C pyrolysis. As shown in Figure 4.34 (b), after 1300°C treatment, peaks for Si particles disappeared. Three peaks for β -SiC enlarged as fibers were treated at elevated temperatures. Compared to XRD patterns of CP5 fiber (see Figure 4.19), SiC peaks of CS9 fibers are slightly larger than those of CP fibers. The difference seems to be on the ridge of each XRD peak. Peaks of CS9 fibers, especially after 1500°C treatment, have an additional sharp portion on the top of the XRD peaks of CP5 fibers. This portion must be attributed to the SiC phase created by the carbothermal reaction between Si particles and excess carbon. Crystallite sizes were calculated using the Scherrer's formula. Table 4.16 summarizes the results of this crystallite size

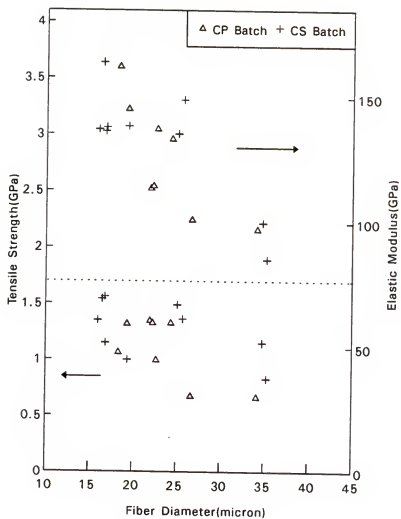


Figure 4.34 Tensile Strength and Elastic Modulus of CP (PCS) and CS (PCS + Si) Fiber Batches after 1000°C Pyrolysis

Intensity (full scale = 1000)

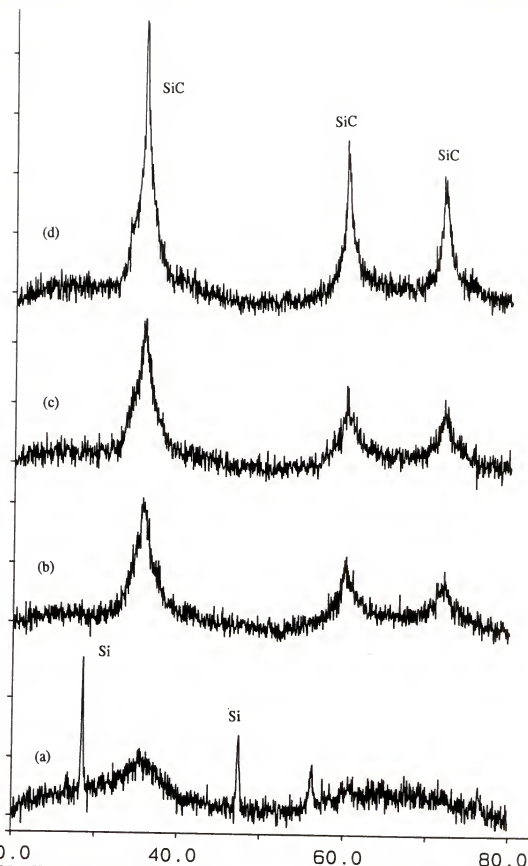


Figure 4.35 X-ray Diffraction Patterns of CS9 Fibers (DC PCS-SZ + 14 w/o Si): Effect of Heat-treatment Temperature (a) As-pyrolyzed, (b) after 1300°C Treatment, (c) after 1400°C Treatment and (d) after 1500°C Treatment

Table 4.16 Summarized XRD Results of CP5 (DC PCS-SZ) and CS9 (DC PCS-SZ + 14 w/o Si) Fibers: Effect of Si Incorporation on Crystallinity

fiber batch	crystalline phase	crystalline size (Å)			
		as-pyrolyzed	after 1300°C treatment	after 1400°C treatment	after 1500°C treatment
CP5	Si	--	--	--	--
	SiC(COP [@])	NA*	26.5	31.4	35.4
	SiC(Si)	--	--	--	--
CS9	Si	299	--	--	--
	SiC(COP)	NA	29.0	32.0	36.7
	SiC(Si)	--	NA	NA	160

* NA denotes that crystallite size could not be measured reliably from XR spectr due to broad and small peaks.

@ COP denotes DC PCS-SZ polymers

calculation. The SiC peak of CS9-15 fibers at $2\theta = 35.6^\circ$ were resolved into two peaks: one for SiC derived from copolymers and the other for SiC derived from the carbothermal reaction. The crystallite size of incorporated Si particles was calculated to be 300 Å. The crystallite size of SiC phases from copolymers ranged 26 to 37 Å. However, the size of SiC from carbothermal reaction was rather large (~ 160 Å). Considering that the strength of polycrystalline materials is inversely proportional to the grain size (Her89), obtaining additional SiC phases of large crystallite size in the fibers may not be desirable. The large grain size of reaction-derived SiC might be related to the large crystallite size of starting Si particles.

Figure 4.36 shows TEM micrographs of CS3 fibers, as-pyrolyzed and after 1300°C treatment. The edge region of a Si particle appeared to be spread into small pieces after 1000°C pyrolysis, as shown in Figure 4.36(a). Electron diffraction patterns [see Figure 4.36(b)] indicated that the central region is still a single crystalline face-centered-cubic silicon. The ratio of distance between long axis and short axis was measured to be 0.61, which matched that between reciprocal indices (111) and (022) seen by beam direction of [211]. Therefore, the Si particles were not involved in the carbothermal reaction at this point. After 1300°C treatment, the particle was further spread out into tiny pieces [see Figure 4.36(c)]. Electron diffraction [Figure 4.36(d)] gave an annular ring pattern which indicated that it was polycrystalline. Since peaks for Si all disappeared after 1300°C treatment in the XRD spectrum, the polycrystalline phase must be SiC. TEM micrographs of CS3-14 and CS3-15 fibers had similar features to those of CS3-13 fibers except that a treatment at higher temperatures gave a larger

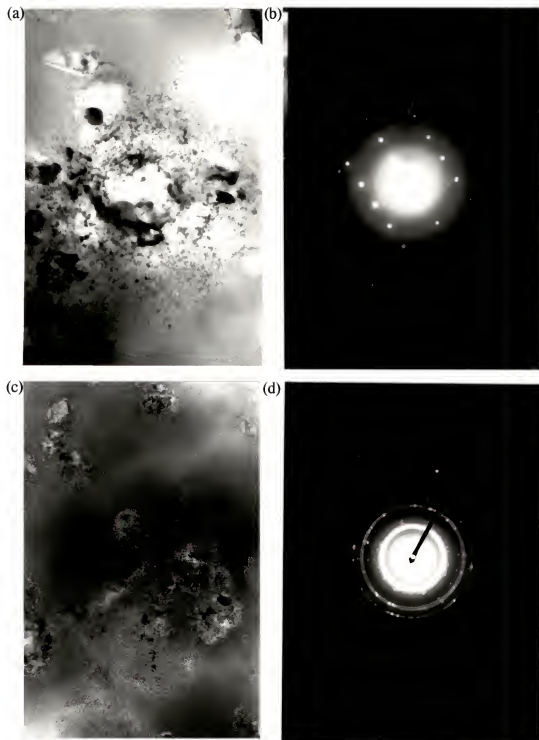


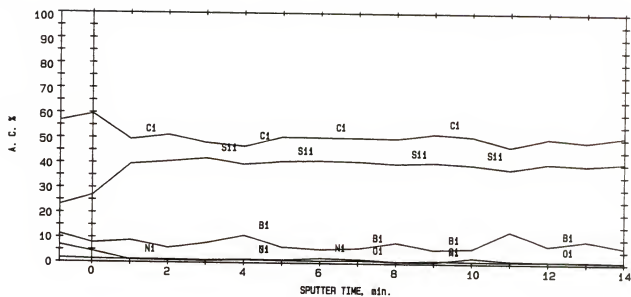
Figure 4.36 TEM Micrographs of CS3 Fibers (DC PCS-SZ + 14 w/o Si): (a) Bright Field Image and (b) Electron Diffraction Pattern after Pyrolysis, (c) Bright Field Image and (d) Electron Diffraction Pattern after 1300°C Treatment

spreading of particles.

Tensile properties of CS fibers were expected to be better as the carbothermal reaction proceeds, as compared to as-pyrolyzed fibers. The actual results showed that this expectation was wrong. CS3 and CS4 fibers became fragile when they were treated at 1400°C. Tensile strength of CS6, CS8 and CS9 fibers was slightly reduced after 1400°C treatment. CS9 fibers were fragile after 1500°C treatment. CS11 fibers had poor uniformity of fiber diameter so that their measured tensile properties might not be as dependable as other data. The changing pattern of fiber elastic modulus versus the treatment temperature was not consistent. A treatment at a higher temperature increased the elastic modulus of CP8 and CP9 fibers, decreased that of CS4 and CS6 fibers, and did not change that of CS3 fibers.

CS12 to CS14 fibers were prepared with PC138. The mixture solution was provided by Dr. Toreki. It contained PSZ of 13.4 w/o, DCP of 1.6 w/o and spinning aid (poly-isobutylene: PIB) of about 1 w/o. CS13 (Si = 20 w/o) and CS14 (Si = 25 w/o) fibers spun well. SAM analysis was performed to measure the change of stoichiometry (Si : C ratio) by Si particle incorporation. Figure 4.37 illustrates depth profiles, via atomic concentration of elements, of cross-sections of as-pyrolyzed CP6 and CS14 fibers. Carbon was rich throughout the 14 minute-depth in CP6 fiber. CS14 fibers containing 25 w/o of Si particles turned out to have a ratio of silicon to carbon greater than one. Quantitative analysis from SAM depth profiles, however, was not recommended.

(a)



(b)

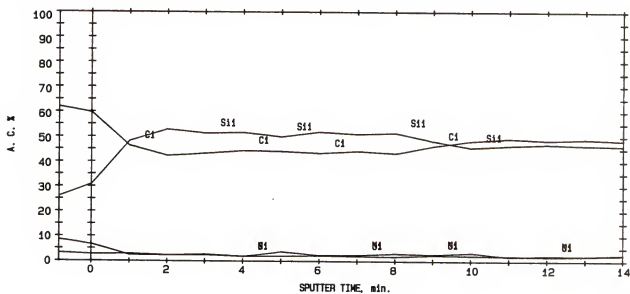


Figure 4.37 Auger Electron Spectra of (a) CP6 (PCS) and (b) CS14 (PCS + 25 w/o Si) Fibers after 1000°C Pyrolysis

Table 4.17 summarizes measured tensile properties of CS12 to CS14 fibers. CS13 and CS14 fibers had good as-pyrolyzed tensile strength (1.6 to 1.7 GPa) and elastic modulus (173 to 181 GPa). However, tensile properties of CS13 and CS14 fibers dropped to a great extent even after 1200°C treatment. These fibers became very weak after 1500°C treatment. Figure 4.38 summarizes XRD pattern change of CS14 fibers as treatment temperature increased. XRD peaks for Si were present with reduced intensity after 1300°C treatment [see Figure 4.39(c)]. Si peaks all disappeared after 1400 or 1500°C treatment. For CS9 fibers, Si peaks disappeared after 1300°C treatment. The difference was attributed to the Si content. CS14 fibers contained more Si particles (25 w/o) than CS9 fibers (14 w/o) so that CS14 fibers needed more time or higher temperature to complete the reaction than CS9 fibers. After 1500°C treatment, CS14 fibers had much more crystalline SiC than CS9 fibers. Figure 4.39 and 4.40 shows SEM micrographs of surfaces of CS11 and CS14 fibers, as-received and after 1800°C treatment. As-pyrolyzed CS14 fibers had a rougher surface than CS11 fibers, due to a higher content of Si particles. CS11-18 fibers were porous. Compared to CS11-18 fibers, CS14-18 fibers were extremely porous and their surface was covered with crystallites. Cross-sections of CS14-18 fibers had the same morphology as their surface; rough and porous.

SEM measurements of CS fibers revealed that CS fiber surfaces became rougher and cross-sections became more porous as they were treated at higher temperatures. The porous structure might be attributed to the size ($\sim 0.15 \mu\text{m}$) of Si particles, which led to a localized volume-shrinking carbothermal reaction. It was suggested to increase the

Table 4.17 Tensile Properties of CS Fibers (UF PCS-PSZ + Si): CS12 to CS14

fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
12	14	29.0 ± 4.3	1.17 ± 0.38	146.8 ± 34.9	8.0 ± 1.4
13	15	16.9 ± 1.6	1.73 ± 0.37	181.2 ± 22.2	9.6 ± 1.8
13-12	14	19.6 ± 3.1	0.91 ± 0.24	170.2 ± 26.2	5.4 ± 1.3
13-15	13	17.5 ± 2.2	0.42 ± 0.11	170.8 ± 18.0	2.5 ± 0.6
14	15	17.0 ± 2.0	1.62 ± 0.30	172.6 ± 33.4	9.5 ± 1.4
14-12	14	15.3 ± 2.3	0.87 ± 0.20	141.5 ± 20.8	6.3 ± 1.7
14-13	13	16.2 ± 1.9	0.98 ± 0.28	160.4 ± 17.1	6.1 ± 1.4
14-15	10	17.0 ± 0.8	0.32 ± 0.07	133.8 ± 15.9	2.4 ± 0.5
14-58	--				
14B	10	25.5 ± 2.4	1.00 ± 0.32	152.1 ± 33.8	6.6 ± 2.2

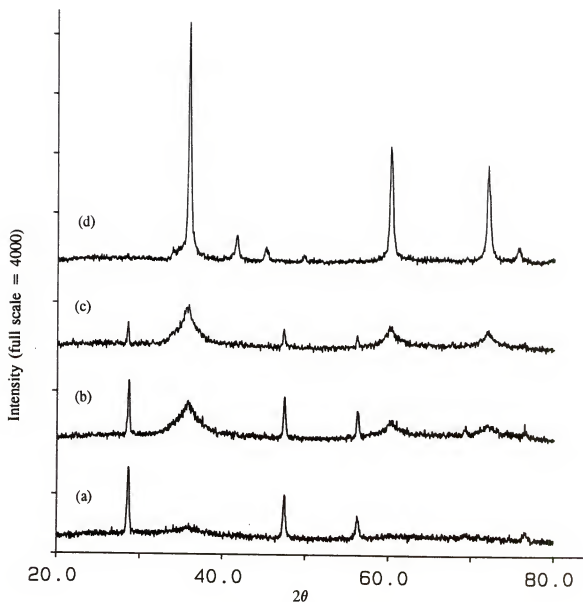


Figure 4.38 X-ray Diffraction Patterns of CS14 Fibers (UF PCS-PSZ + 25 w/o Si): Effect of Heat-treatment Temperature (a) As-pyrolyzed, (b) after 1200°C Treatment, (c) after 1300°C Treatment and (d) after 1500°C Treatment

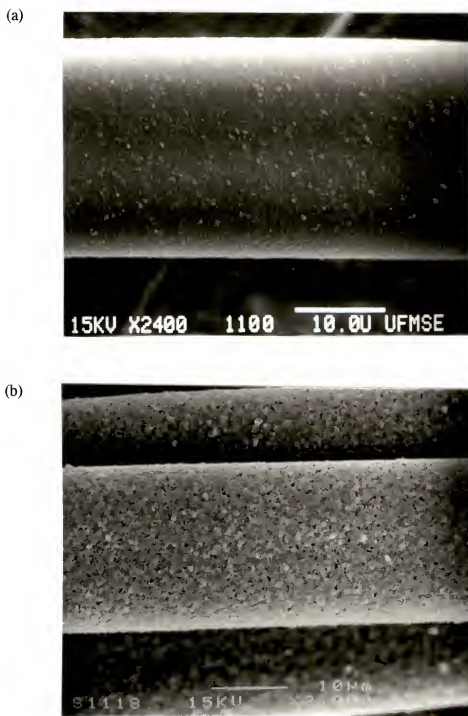
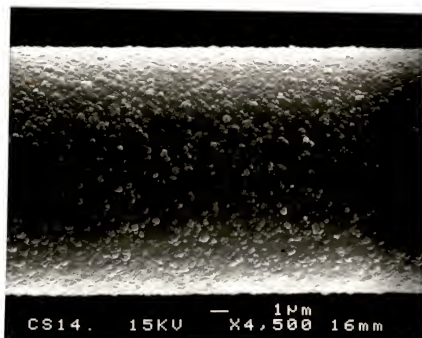


Figure 4.39 SEM Micrographs of CS11 Fibers (DC PCS-SZ + 14 w/o Si): (a) As-pyrolyzed and (b) after 1800°C Treatment

(a)



(b)

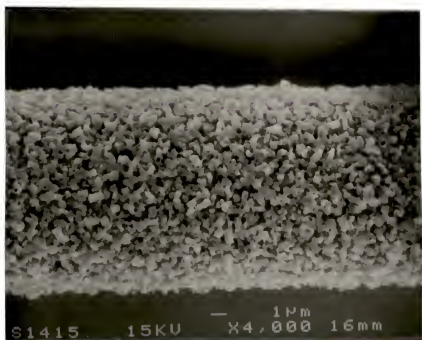
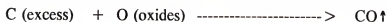
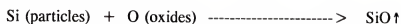


Figure 4.40 SEM Micrographs of CS14 Fibers (UF PCS-PSZ + 25 w/o Si): (a) As-pyrolyzed and (b) after 1800°C Treatment

temperature to 1420°C (which is 10°C above the melting temperature of silicon) as fast as possible to melt Si particles and spread them out as liquid for improved uniformity before the reaction occurs. The greatest heating rate of Centorr furnace was 54°C per minute and four fiber batches (CS6, CS11, CS13 and CS14) were treated using this rate. It took 19 minutes to heat them up from 400 to 1420°C. Fibers were then heated at 1420°C for an hour. SEM examination did not detect any difference caused by the fast heating. Fibers treated at 1420°C by the fast heating had fewer pores in their cross-section. No significant difference was appreciated in tensile properties. It seems that the heating rate of 54°C per minute was not enough to spread out incorporated silicon uniformly.

As-received Si particles were found, via NAA measurement, to have an oxygen content of 2.8 w/o (see Table 4.18). The oxygen content was attributed to the Si-O layer on the outermost surface of Si particles. Assuming that the oxide layer on Si particles of different sizes has the same thickness, the oxygen content in fractionated Si solution was calculated to be about 12 w/o. The porosity development in CS fibers after treatments at elevated temperatures was attributed primarily to two factors: volume reduction by the carbothermal reaction and oxidation reactions by oxide layers on Si particles. The first mechanism definitely has an effect as long as there is a reaction. Assuming densities of those substances such as $\rho_{\text{Si}} = 2.33$, $\rho_{\text{C,graphite}} = 2.25$, $\rho_{\text{C,amorphous}} = 1.95$, and $\rho_{\text{SiC}} = 3.2 \text{ g/cm}^3$, the volume reduction by the carbothermal reaction can be as large as about 40%. The volume reduction would leave some voids around particles. The second mechanism was due to the oxygen causing reactions such as shown

below, to produce volatile species:



It is yet to be determined which factor is more responsible for the porosity development of the heat-treated fibers.

CS6B and CS14-series fibers were measured via NAA to identify their elemental compositions. Table 4.18 summarizes NAA analysis results. As-pyrolyzed CS6B and CS14 fibers include significant oxygen (3.8 to 4.5 w/o). Considering that the oxygen content of PCS was less than 2 w/o, the large portion of oxygen must have been originated from Si particles of heavier oxygen content. Assuming the nitrogen content was 1 w/o, the chemical formula of CS14 fibers estimated from NAA results is $\text{Si}_{1.00}\text{C}_{1.15}\text{O}_{0.10}\text{N}_{0.03}$. This result was not consistent with SAM analysis results of CS14 fibers, which indicated that silicon was richer than carbon in CS14 fibers, but both measurements showed approximately equal levels of silicon and carbon. CS14-13 fibers had less oxygen and greater Si content than CS14 fibers. This might have happened through reaction between carbon and oxygen to produce CO gas as a product. CS14-15 and CS14-58 fibers gave results which were not consistent with the above explanation. One of the possible reasons was: CS14-15 and CS14-58 were sent out for NAA analysis some time after CS14 and CS14-13 were measured via NAA. It was reported that second sets of NAA measurements (for CS14-15 and CS14-58) were performed with poor reproducibility. This implies that NAA results of CS14-15 and CS14-58 fibers may not be as dependable.

Table 4.18 Summarized Results of Neutron Activation Analysis

sample name	composition (w/o)		
	oxygen	silicon	others
Si (aged)	2.37 ± 0.01	97.1 ± 0.61	0.53
Si (new)	0.82 ± 0.01	97.8 ± 0.5	1.38
SiC (aged)	1.41 ± 0.05	64.0 ± 0.6	34.59
CS6B	3.78 ± 0.02	57.4 ± 0.51	38.82
CS14	4.54 ± 0.07	61.7 ± 0.5	33.76
CS14-13	3.79 ± 0.08	63.8 ± 0.7	32. 41
CS14-15	1.63 ± 0.07	59.6 ± 0.8	38.77
CS14-58	3.31 ± 0.05	61.9 ± 0.6	34. 79

Table 4.19 summarizes the measured density of CS14-series fibers. The density of as-pyrolyzed CS14 fibers (2.32 g/cm^3) was lower than that of CP fibers ($\sim 2.45 \text{ g/cm}^3$) since the density of Si particles is 2.33 g/cm^3 . As expected from SEM micrographs, the density of CS14 fibers was very low after 1500°C treatment. This is due to rough surface as well as the porous microstructure. Table 4.20 summarizes BET results for CS fibers. The surface area of CS fibers increased gradually up to the 1300°C treatment. This area became very large (1.1 to $2.8 \text{ m}^2/\text{g}$) after 1500°C treatment. The measured surface area of UF 127-12 SiC fiber batch after 1500°C treatment was less than $0.5 \text{ m}^2/\text{g}$ while that of Nicalon fibers was around $4.0 \text{ m}^2/\text{g}$ (Tore92).

Washing of Si particles in concentrated HF ($\sim 50\%$) did not work out well. This was due to a severe flocculation occurring right after Si particles were in contact with the acid. Even a few grams of Si particles caused a flocculation in one hundred grams of acid. Two batches of CS fibers were washed with concentrated acids. The effect of fiber soaking in boric acid on the surface morphology was examined as well. Figure 4.41 shows the surface change caused by soaking of CS fibers in HF. A number of tiny craters were seen, which were left after Si particles were removed from the surface. Treated fibers were characterized by tensile testing, SEM and XRD. No difference was observed in tensile properties or SEM micrographs between four different treatments.

Fibers from PCS-based Polymers with Si Particles and Decaborane

It was apparent that the stoichiometry was enhanced by incorporating Si particles in the polymer-derived SiC fibers. However, CS fibers after heat-treatment at elevated

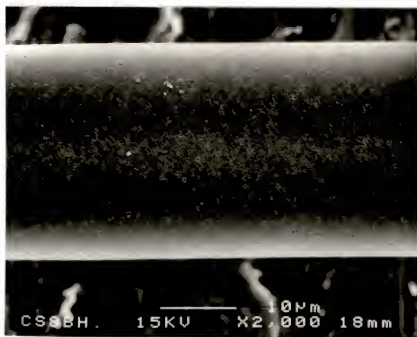
Table 4.19 Measured Density of CS14 Fibers (UF PCS-PSZ + 25 w/o Si)

batch name	fiber density (g/cm ³)	
	weight measurement	pycnometer
CS14	2.318	2.326
CS14-13	2.461	2.462
CS14-15	2.206	2.233

Table 4.20 Summarized Results of BET Analysis of CS Fibers (PCS + Si)

batch name	sample amount (g)	BET surface area (m ² /g)	
		#1	#2
CS8	0.3078	0.1943	0.1946
CS8-15	0.0695	2.8420	2.8804
CS9	0.2700	0.1904	0.1929
CS9-13	0.1283	0.6469	0.6699
CS9-15	0.0824	1.0898	1.1047
CS14	0.1545	0.2557	0.2792
CS14-13	0.1422	0.3563	0.3708
CS14-15	0.1386	1.6112	1.6319

(a)



(b)

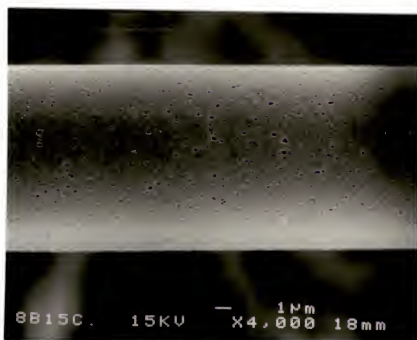


Figure 4.41 SEM Micrographs of HF-washed CS8 Fibers (DC PCS-SZ + 14 w/o Si):
 (a) As-washed and (b) after 1500°C Treatment

temperatures suffered from the development of a porous microstructure and a rough and grainy surface. To make the Si particle incorporation approach useful, it was necessary to develop a method to close up all pores in the fibers or to prevent pores from being created. Hence, decaborane was incorporated with CS fibers. Fibers from decaborane incorporated CS fiber compositions are referred to as *CSD* fibers. DC PCS and UF PCS (PC143 and PC144) were studied.

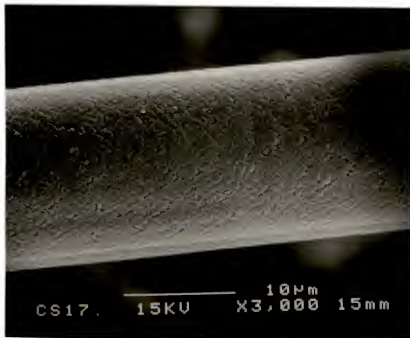
Similar to CPD fibers, PCS solutions including SZ or PSZ caused gelation problems when decaborane was added to them. CSDi and CSDj compositions did not allow easy spinning due to gelation during evaporation. From the experimental point of view, it was extremely difficult to notice gelation occurring during evaporation because the mixture solutions for CSD fibers were opaque. Gelation was not noticeable until when the viscous mixture (after evaporation) was being transferred to the spinneret. If the mixture did not flow, then spinning was not possible.

Table 4.21 summarizes measured tensile properties of CSD fibers. CSD17 fibers had decent as-pyrolyzed tensile strength (2.0 GPa) and elastic modulus (184 GPa), compared with SiC fibers derived from DC PCS. After 1800°C treatment, CSD17 fibers retained good tensile strength (1.5 GPa: 75% of as-pyrolyzed strength). Moreover, elastic modulus increased to a great extent (283 GPa) after 1800°C treatment. Figure 4.42 illustrates SEM micrographs of CSD17 fiber surfaces, as-pyrolyzed and after 1800°C treatment. CSD17 fibers had a surface typical of as-pyrolyzed CS fibers. Compared to CPD10A-18 fibers [see Figure 4.22 (b)], CSD17-18 fibers had a rougher surface covered with more crystallites. However, the surface backgrounds looked rather

Table 4.21 Tensile Properties of CSD Fibers (PCS + Si + decaborane)

fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
17	14	17.8 ± 1.6	2.02 ± 0.59	184.3 ± 40.2	10.9 ± 1.8
17-18	14	16.1 ± 1.6	1.45 ± 0.35	283.2 ± 15.5	5.1 ± 0.7
19	15	16.2 ± 1.2	1.81 ± 0.39	192.0 ± 12.0	9.4 ± 1.9
19-18	15	14.6 ± 0.9	1.22 ± 0.24	241.0 ± 8.7	5.1 ± 1.0
20	15	14.5 ± 3.6	1.61 ± 0.45	211.1 ± 42.5	7.6 ± 1.8
20-18	17	13.8 ± 0.8	1.11 ± 0.21	267.3 ± 31.7	4.2 ± 0.6
21	17	14.3 ± 0.9	1.67 ± 0.22	190.0 ± 11.9	8.8 ± 1.1
21-18	13	12.9 ± 0.5	1.48 ± 0.23	251.1 ± 10.2	5.9 ± 0.8
21F	17	13.1 ± 0.7	1.86 ± 0.21	202.3 ± 17.4	9.2 ± 1.1
21F-18	13	12.1 ± 0.7	1.38 ± 0.30	293.0 ± 13.7	4.7 ± 1.0

(a)



(b)

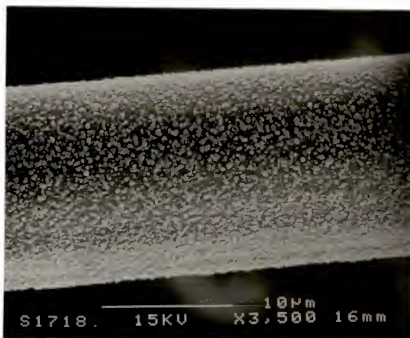
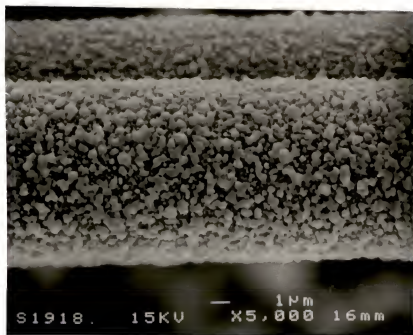


Figure 4.42 SEM Micrographs of CSD17 Fibers (DC PCS-SZ + 14 w/o Si + 1.6 w/o decaborane): (a) As-pyrolyzed and (b) after 1800°C Treatment

dense. As shown in Figure 4.38 and Figure 4.40, CS11-18 and CS14-18 fibers had extremely rough and porous surface morphology. Therefore, decaborane incorporation somehow worked for the densification of CS fibers. The measured density of CSD17 fibers was rather low (2.37 g/cm^3 ; see Table 4.13). After 1800°C treatment, the density increased to 2.92 g/cm^3 . Considering that the theoretical density of crystalline SiC is 3.22 g/cm^3 , the density of CSD17-18 fibers corresponds to 91% densification.

It was speculated that the rough surface of CSD17-18 fibers might be due to a low decaborane content. Fully densified microstructure may require more decaborane. The effect of variation of decaborane content was studied. CSD19 and CSD20 fibers were prepared from PC143 with decaborane contents of 3.2 and 7.5 w/o, respectively. Figure 4.43 shows SEM micrographs of surfaces of CSD19 and CSD20 fibers after 1800°C treatment. They all had rough surface covered with a number of crystallites. CSD20-18 fibers seemed to have smaller crystallites than CSD19-18 fibers. Growth of crystallites was restricted to a greater extent in CSD20 fibers. The results suggested that boron content on the surface of CSD20-18 fibers was still not enough for a good densification at least near the surface. This means either that an increased amount of decaborane needs to be added to polymers or that decaborane on the green fiber surface was too volatile to retain an adequate level of boron during pyrolysis irrespective of the decaborane level. If the latter is the case, addition of more decaborane into the polymer solution would not work effectively. CSD19 and CSD20 fibers had mediocre as-pyrolyzed tensile strength (1.6 to 1.8 GPa). Even though CSD20-18 fibers had a more desirable surface morphology than CSD19-18 fibers, there was no benefit in the tensile

(a)



(b)

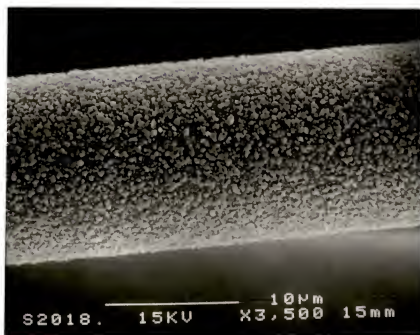


Figure 4.43 SEM Micrographs of (a) CSD19 (UF PCS + 17 w/o Si + 2.7 w/o decaborane) and (b) CSD20 Fibers (UF PCS + 17 w/o Si + 6.4 w/o decaborane) after 1800°C Treatment: Effect of Decaborane Content on Surface Morphology

properties by the high decaborane content. Those fibers had similar tensile strength retention (67 to 69%) and elastic modulus increase (126 to 127%).

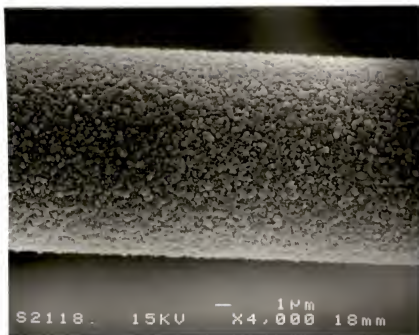
CSD21-series fibers were prepared from PC144 to study the effect of fast pyrolysis. The mixture included Si particles of 14 w/o and decaborane of 7.6 w/o. One half of the green fibers were pyrolyzed by the regular 1000°C temperature profile (CSD21). The other half of the green fibers were pyrolyzed in the following temperature profile (CSD21F):

30°C ----- (2 hours)----- > 1000°C (1 hour hold) ----- (4 hours)----- > 30°C

The hold at 150°C during regular 1000°C pyrolysis profile was to enhance the crosslinking by DCP. The fast heating was intended to reduce the loss of decaborane by vaporization during pyrolysis. The ceramic yield of CSD21F fibers (81%) was slightly higher than that of CSD21 fibers (77%). Figure 4.44 illustrates CSD21 and CSD21F fibers after 1800°C treatment. Even though both fibers had very rough surfaces, CSD21F-18 fibers had fewer surface crystallites than CSD21-18 fibers. Tensile properties of CSD21-series fibers are summarized in Table 4.21. CSD21 and CSD21F fibers did not have as good a pyrolyzed tensile strength (1.7 to 1.9 GPa). CSD21-18 fibers, surprisingly, had a better strength (1.5 GPa) than the better-looking CSD21F-18 fibers (1.4 GPa). Those fibers gave decent strength retention rates (74 to 89%). The elastic modulus of CSD21F fibers was 293 GPa, which was the greatest average value attained in this study or any other fibers produced at UF to date.

Figure 4.45 and Figure 4.46 show graphical comparisons of tensile properties between CPD and CSD fiber batches. Tensile strength and elastic modulus of as-

(a)



(b)

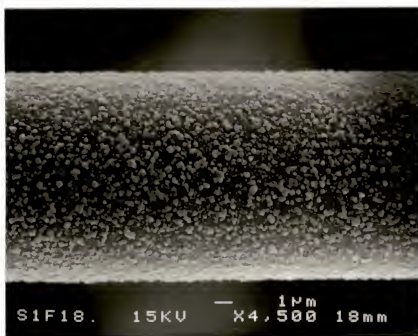


Figure 4.44 SEM Micrographs of (a) CSD21 (UF PCS + 17 w/o Si + 6.6 w/o decaborane) and (b) CSD21F Fibers (fast pyrolysis) after 1800°C Treatment: Effect of Fast Pyrolysis on Surface Morphology

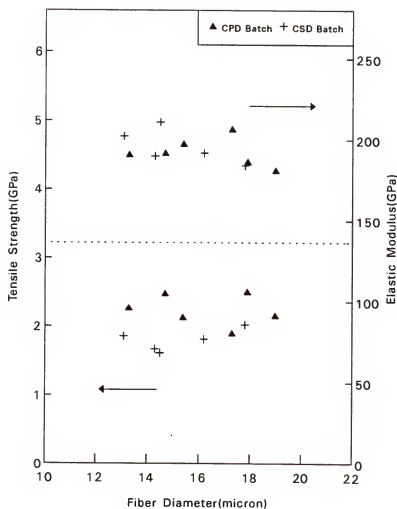


Figure 4.45 Tensile Strength and Elastic Modulus of CPD (PCS + decaborane) and CSD (PCS + Si + decaborane) Fiber Batches after 1000°C Pyrolysis

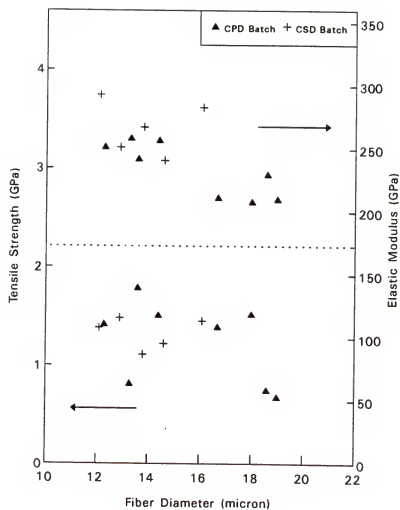


Figure 4.46 Tensile Strength and Elastic Modulus of CPD (PCS + decaborane) and CSD (PCS + Si + decaborane) Fiber Batches after 1800°C Treatment

pyrolyzed CPD and CSD fibers are plotted versus average fiber diameter in Figure 4.45. CPD fiber batches have slightly better tensile strength than CSD batches, while elastic moduli of those batches are about the same. The same type of plot is given in Figure 4.46 for fiber batches after 1800°C treatment. CPD and CSD fibers had similar tensile strength. CSD fibers gave a slightly greater elastic modulus than CPD fibers. The edge of CSD fibers over CPD fibers in the elastic modulus was acquired from additional crystalline SiC by Si incorporation. Figure 4.47 illustrates the correlation of crystallinity with elastic modulus for all fiber batches treated at 1800°C. CSD17-18 fibers had the greatest crystallinity as well as highest elastic modulus among the plotted fiber batches.

Table 4.22 summarizes the results of Weibull modulus calculation for selected CP, CPD, CS and CSD fiber batches. Since there was no duplicate tensile testing, Weibull modulus numbers were rounded off to integer (numbers in the parenthesis were rounded off to the first digit below zero). Only as-pyrolyzed and 1800°C-treated fibers were considered in this calculation. The method to calculate Weibull modulus from tensile strength data was described previously (see pages 17-18). The survival probability $P_s(V)$, was obtained using the following equation:

$$P_s(V) = 1 - \frac{i}{N + 1} \quad i = \text{strength rank}; 1, 2, \dots, N$$

where N = total number of tested specimens. Since the number of fiber specimens was smaller (ranging 11 to 17) than 50 points normally recommended for such analysis, the absolute values of calculated Weibull modulus here may not be of great significance. However, the trend of their changes occurring by a heat-treatment at 1800°C should be

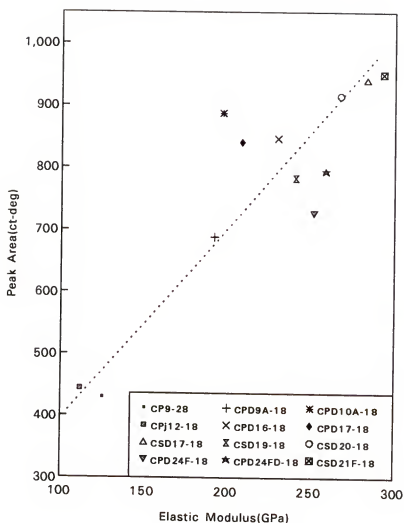


Figure 4.47 Plot of XRD Peak Area versus Fiber Elastic Modulus after 1800°C Treatment

Table 4.22 Weibull Moduli of CP (PCS), CPD (PCS + decaborane), CS (PCS + Si) and CSD (PCS + Si + decaborane) Fibers

class	batch	PCS	# of tests	Weibull modulus
CP	j	PC144	11	3 (2.7)
	j-18		14	1 (1.3)
	k	PC144	13	4 (3.6)
	k-18		14	3 (2.6)
	12	DC PCS	16	4 (3.8)
	12-18		12	2 (2.2)
	14	PC143	13	8 (8.4)
	14N-18		14	3 (3.4)
CPD	17	PC144	16	4 (3.8)
	17-18		13	4 (4.5)
	22	PC143	15	3 (2.7)
	22-18		14	6 (5.6)
	23F	PCD156	16	2 (2.3)
	23F-18		12	4 (3.8)
	23F	PCD156	13	4 (3.7)
	23F-18		16	4 (4.4)
CS	11	DC PCS	14	2 (2.3)
	11-18		11	2 (1.7)
CSD	17	DC PCS	14	3 (3.4)
	17-18		14	4 (4.3)
	21	PC144	17	8 (7.7)
	21-18		13	5 (5.4)

valid for a correlation with the chemical modifications and clear differences are seen in the following plotted data (Figures 4.48 to 4.50) which would not change with added points.

Except for CP14 and CSD21 fibers, most as-pyrolyzed fibers had a Weibull modulus within a narrow range (2.3 to 3.8). Therefore, the chemical modifications (Si particles and/or decaborane incorporation) did not have a significant effect on the reliability of as-pyrolyzed fibers. Weibull moduli of CP and CS fiber batches decreased to a great extent after a 1800°C treatment in all cases. On the other hand, Weibull moduli of CPD and CSD batches increased remarkably after 1800°C treatment. The only exception for the latter occurred for CSD21 batch whose as-pyrolyzed fibers had an extremely high Weibull modulus (7.7). Nevertheless, that of CSD21-18 fibers was relatively high (5.4).

Figure 4.48 and 4.49 show typical Weibull plots of fibers with and without decaborane (CPk and CPD22), as-pyrolyzed and after 1800°C treatment. CPk-18 fibers had not only much lower strength but also a slightly smaller slope (m), Weibull modulus than CPk fibers (see Figure 4.48). CPD22 fibers had a slightly lower strength, but had steeper slope (i.e., greater Weibull modulus) after 1800°C treatment (see Figure 4.49). It seems obvious that the decaborane incorporation to CP or CS fiber dopes not only enhanced the tensile properties of fibers but also improved the reliability of fibers, after 1800°C heat-treatment. As shown in Figure 4.50, CSD21-18 fibers (the only decaborane-incorporated fiber batch for decreased Weibull modulus after 1800°C treatment) retained the Weibull modulus to a great extent. The decrease in the Weibull

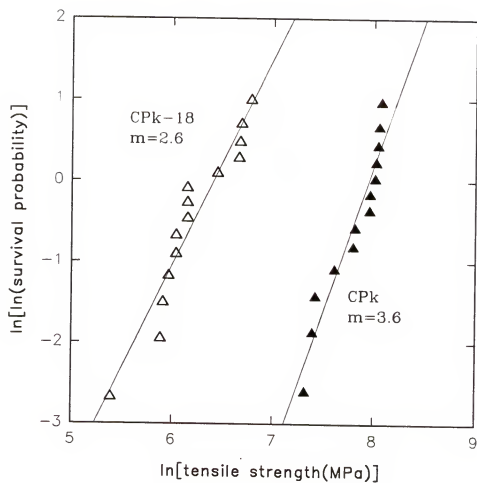


Figure 4.48 Weibull Plot of CPk (UF PCS-PSZ) and CPk-18 Fibers

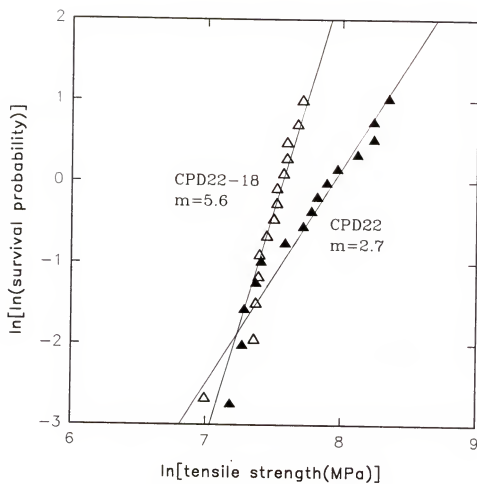


Figure 4.49 Weibull Plot of CPD22 (UF PCS + 3.4 w/o decaborane) and CPD22-18 Fibers

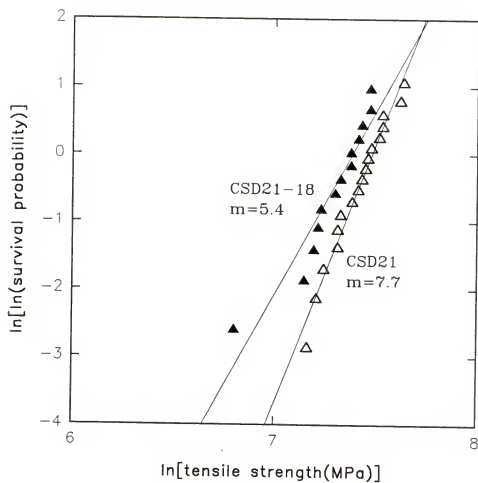


Figure 4.50 Weibull Plot of CSD21 (UF PCS + 17 w/o Si + 6.6 w/o decaborane) and CSD21-18 Fibers

modulus by the 1800°C treatment (from 7.7 to 5.4) was mainly caused by one data point at the lowest strength.

Fibers from PCS-SX Copolymers with/without Decaborane

CPD fibers demonstrated that decaborane incorporation could enhance the thermostability of polymer-derived SiC fibers to a great extent. The highest elastic modulus among CPD fiber batches was attained by CPD23F-18 fibers (257 GPa). Even the highest elastic modulus is much smaller than that of either Textron SCS-8 SiC fibers (400 GPa) or SiC whiskers (580 GPa). This is presumably due to the high excess carbon content in the fibers. More excess carbon must be burnt out to attain a higher elastic modulus for these polymer-derived SiC fibers. However, the oxygen content in PCS or SZ is not high enough. One potential route was to introduce excess oxygen and consume the excess carbon by the following reaction:



One of the several possible ways for additional oxygen introduction was the use of SX for copolymerization with DC PCS instead of SZ.

Fibers prepared from DC PCS-SX copolymers with or without decaborane are referred to as *CY* fibers. *CY1* fibers were processed with decaborane while *CY2* fibers were fabricated without decaborane. As observed in other fiber batches, decaborane incorporation tended to increase the ceramic yield of fibers (70.1% of *CY1* over 65% of *CY2* fiber). The surface of as-pyrolyzed *CY1* fibers was similar to that of CP fibers. *CY3* fibers were prepared with an increased SX content (30 w/o). The oxygen content

of CY3 fibers was calculated to be approximately 5.6 w/o. CY4 fibers were produced with Si particles as well as with decaborane.

Table 4.23 summarizes measured tensile properties of CY fiber batches. Even though fibers spun well, as-pyrolyzed tensile strength of CY fibers was rather low (1.0 to 1.3 GPa) due to the small rupture strain (0.6 to 0.7%). Si-incorporated CY4 fibers had even poorer strength (0.7 GPa). Tensile strength retention rates of CY1 and CY2 fibers after a 1500°C treatment were about the same (65%). Therefore, there was no appreciable effect of boron incorporation on the thermomechanical stability of fibers up to 1500°C treatment. Decaborane incorporation made some difference when fibers were treated at 1800°C. CY1B-18 fibers had a reasonable tensile strength retention rate (74%) while CY2-18 fibers were not testable for tensile properties. CY3 fibers had good strength retention rate (55%) up to 1500°C treatment but were not testable after 1800°C treatment.

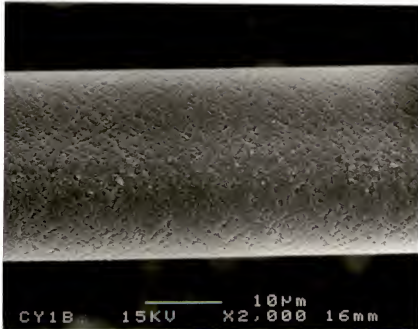
Figure 4.51 illustrates SEM surface morphology of CY1 fibers, as-pyrolyzed and after 1800°C treatment. CY1B-18 fibers had rough surfaces fully covered with crystallites. Some crystallites were as large as one micron. Cross-sections of CY1B-15 had no apparent pores. The grain size increased slightly. EMP was employed for chemical identification of the crystallites on the surface of CY1B-15 fibers. The findings from the EMP results, however, were not informative. Thus, the EMP results are not discussed any further here.

Figure 4.52 summarizes XRD patterns of CY1-series fibers. No oxygen-involving crystalline phase was created. β -SiC was the only crystalline phase detected

Table 4.23 Tensile Properties of CY Fibers (DC PCS-SX with/without decaborane)

fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
1	14	19.6 ± 2.9	1.09 ± 0.32	178.3 ± 35.8	6.2 ± 2.0
1B	11	21.5 ± 2.5	1.03 ± 0.26	176.3 ± 39.7	5.9 ± 1.0
1B-15	12	18.1 ± 1.5	0.66 ± 0.18	173.1 ± 24.4	3.9 ± 1.0
1B-18	14	15.3 ± 1.8	0.76 ± 0.30	159.5 ± 37.9	4.7 ± 1.2
2	14	19.0 ± 2.6	1.03 ± 0.42	173.7 ± 48.6	5.9 ± 1.5
2-15	12	21.8 ± 1.8	0.65 ± 0.13	150.9 ± 23.3	4.3 ± 0.8
3	11	16.7 ± 1.8	1.27 ± 0.58	184.5 ± 30.7	6.8 ± 2.6
3-13	11	15.4 ± 1.5	1.11 ± 0.40	184.4 ± 31.2	5.9 ± 1.6
3-15	11	12.3 ± 1.3	0.69 ± 0.25	198.9 ± 29.6	3.4 ± 0.9
4	12	17.5 ± 2.0	0.73 ± 0.24	161.3 ± 27.7	4.5 ± 1.2
4-15	10	16.9 ± 2.0	0.41 ± 0.17	175.2 ± 43.2	2.4 ± 1.0

(a)



(b)

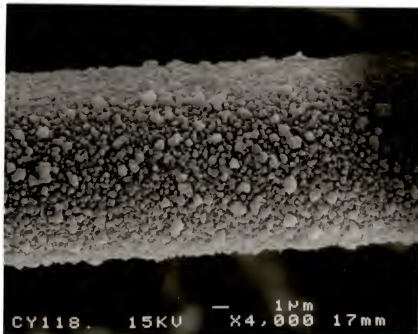


Figure 4.51 SEM Micrographs of CY1 Fibers (DC PCS-SX + 1.5 w/o decaborane):
(a) As-pyrolyzed and (b) after 1800°C Treatment

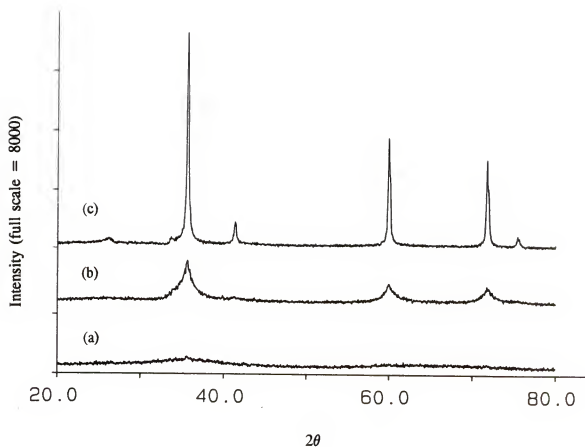


Figure 4.52 X-ray Diffraction Patterns of CY Fibers (DC PCS-SX + 1.5 w/o decaborane): (a) As-pyrolyzed, (b) after 1500°C Treatment and (c) after 1800°C Treatment

in XRD spectra of CY1B-15 and CY1B-18 fibers. The intensities of the SiC (111) peak at $2\theta = 35.6^\circ$ of CY1B-15 and CY1B-18 fibers were about the same as those of CPD fibers after 1500°C and 1800°C treatment. Decaborane-derived boron must have been working as a crystallization aid for CY1 fibers much as it did for CPD fibers. Figure 4.53 shows the depth profile in atomic concentration of CY1 fibers measured by SAM. Compared to CP6 fibers [see Figure 4.38(a)], CY1 as-pyrolyzed fibers had a poor stoichiometry (carbon : silicon = 1.62). One repeat unit of SX has three carbons and one silicon. The stoichiometry of CY1 fibers became poorer than CP6 fibers probably because more than one carbon per one oxygen survived the pyrolysis.

The approach of SX incorporation in PCS to improve the stoichiometry of SiC fibers may not be very promising due to several problems. First, a CY fiber batch with decent as-pyrolyzed tensile strength has not been prepared. Because of its poor initial C to Si ratio, SX incorporation may make the stoichiometry of as-pyrolyzed fibers even worse.

Fibers from PCS-SZ Polymers with SiC Particles

SiC particles were incorporated with DC PCS-SZ copolymers. Fibers derived from SiC-incorporated copolymers are referred to as CX fibers. Aged α -SiC particles were used for CX1 whereas β -SiC particles of 99.5 w/o purity were used for CX3 fibers. Table 4.24 summarizes measured tensile properties of CX fibers. CX1 fibers had good as-pyrolyzed tensile strength (1.7 GPa) and excellent elastic modulus (243 GPa). However, after they were treated at elevated temperatures, CX1 fibers had poor tensile

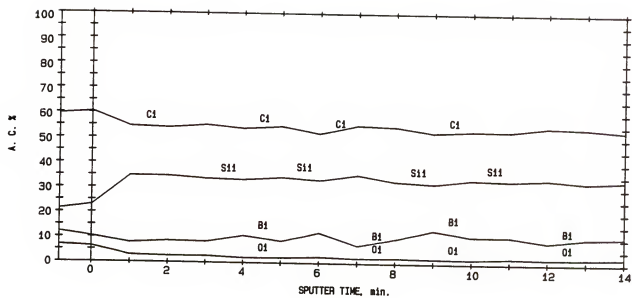


Figure 4.53 Auger Electron Spectrum of As-pyrolyzed CY1 Fibers (DC PCS-SX + 1.5 w/o decaborane)

Table 4.24 Tensile Properties of CX Fibers (DC PCS-SZ + SiC)

fiber batch name	# of tests	fiber diameter (μm)	tensile strength (GPa)	elastic modulus (GPa)	rupture strain (10^{-3})
1	11	15.1 ± 1.8	1.70 ± 0.53	242.5 ± 59.2	7.0 ± 1.4
1-12	14	17.1 ± 1.9	1.29 ± 0.47	173.8 ± 37.8	7.4 ± 1.6
1-15	10	16.9 ± 2.7	0.43 ± 0.15	195.4 ± 68.7	2.2 ± 0.4
1B	14	29.7 ± 4.4	1.23 ± 0.46	130.7 ± 41.2	9.4 ± 1.7
1B-15	12	29.1 ± 3.6	0.42 ± 0.14	125.4 ± 38.6	3.3 ± 0.9
2	stuck fibers				
3	13	22.7 ± 2.6	0.59 ± 0.19	161.7 ± 37.0	3.6 ± 0.8
3-15	15	19.5 ± 2.9	0.15 ± 0.07	122.1 ± 46.6	1.2 ± 0.2

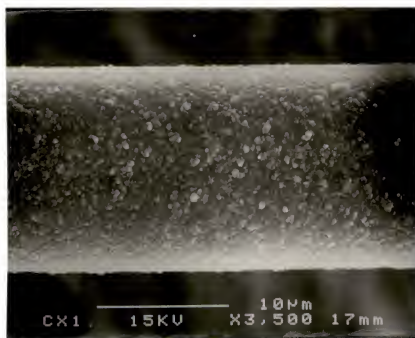
properties. CX3 fibers were processed with decaborane. They had poor as-pyrolyzed tensile properties. Figure 4.54 shows SEM surface morphology of CX1 fibers, as-pyrolyzed and after 1500°C treatment. As-pyrolyzed fibers had a surface of typical CS fibers. CX1-15 fibers had rough surface covered with particles. Some particles are as large as one micron. The surface roughness of CX1-12 fibers was similar to that of CX1 fibers. NAA measured the oxygen content of aged α -SiC was 1.4 w/o. The actual oxygen content in fractionated SiC particles would be about 6.0 w/o. The oxygen would have caused following reactions to form volatile product and leave porous microstructure behind:



Figure 4.55 summarizes XRD patterns of CX1-series fibers. As-pyrolyzed CX1 fibers had five peaks which corresponded to crystalline α -SiC. Compared to that of PCS-derived β -SiC, CX1-15 fibers had large shoulder peaks on both sides of the peak at $2\theta = 35.6^\circ$. This means that the newly formed SiC (from DC PCS-SZ) tends to be α -SiC when the crystallization occurs on the incorporated α -SiC particles.

As mentioned earlier, the settling of β -SiC particles was less than satisfactory so that the SiC particle solution used for CX3 fibers was obtained by a 30 minute settling. CX3 fibers had extremely low tensile strength. CX3-15 fibers were observed via an optical microscope to have a very rough surface. It was found that SiC fibers with good strength would be hardly produced from the incorporation of coarse particles.

(a)



(b)

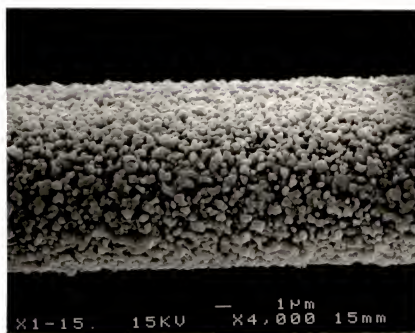


Figure 4.54 SEM Micrographs of CX1 Fibers (DC PCS-SZ + 30 w/o SiC): (a)As-pyrolyzed and (b) after 1500°C Treatment

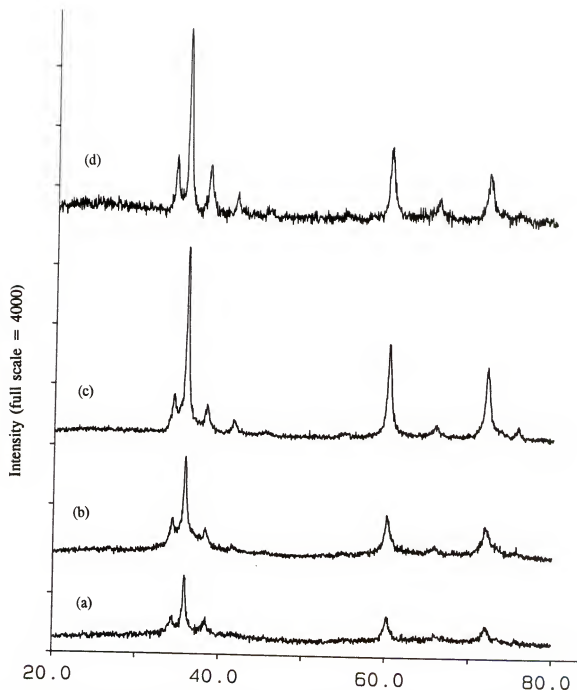


Figure 4.55 X-ray Diffraction Patterns of CX1 Fibers (DC PCS-SZ + 30 w/o SiC): Effect of Heat-treatment Temperature (a) As-pyrolyzed, (b) after 1200°C Treatment, (c) after 1500°C Treatment and (d) As-received α -SiC Particles

CHAPTER 5 CONCLUSIONS

1. Polymerization of silazane (SZ) and siloxane (SX) monomers and copolymerization of Dow Corning polycarbosilane (DC PCS) with SZ or SX was well accomplished via a solution polymerization method with predetermined reaction conditions: 130°C for 18 hours. Gelation tended to occur during polymerization when either the monomer concentration or the initiator (dicumyl peroxide) content was high.

2. Silicon particles reacted with excess carbon in polymer dopes, which were subsequently reacted to produce additional SiC when the mixture was heat-treated at 1350 to 1500°C. The reaction temperature was near the melting temperature of silicon, 1410°C. HfSi₂ and TiSi₂ particles also reacted with excess carbon in polymer dopes to form HfC and TiC as well as SiC at 1350 to 1500°C. The reaction temperature was substantially lower than the melting temperatures of HfSi₂ and TiSi₂, which are 1680 and 1720°C.

3. Decaborane was studied as a boron additive to DC PCS-derived SiC. After 1000°C pyrolysis, decaborane high-dope (15 w/o) samples retained a high boron content (2.3 and 6.6 atomic percent for SX and SZ incorporation, respectively). However, the boron-containing ceramic compounds were all amorphous after pyrolysis. The ceramic yield of decaborane alone after 1000°C pyrolysis was almost zero. Decaborane interacted with amine in SZ to form a hazy complex.

4. CP fibers, derived from PCS-based polymers, had a good strength retention up to 1400°C. Fibers tended to have a greater tensile strength after 1400°C treatment than that of as-pyrolyzed fibers. When CP fibers were treated at 1500°C or higher, tensile properties decreased to a great extent accompanied by development of a porous microstructure. Most CP fibers were too weak to test for tensile properties after a 1800°C treatment.

5. Decaborane incorporation increased the crosslinking in PCS-SZ or PCS-PSZ polymers by a reaction presumably with the amine group in SZ. This reaction reduced the minimum amount of SZ required for adequate infusibility of green fibers made from DC PCS during pyrolysis. Decaborane incorporation also increased the ceramic yield of green fibers by a few percent.

6. Decaborane incorporation to CP fibers (CPD fibers) resulted in a remarkable enhancement of thermomechanical stability to 1800°C. SEM analysis of CP and CPD fibers after 1800°C treatment has found significant effects. No appreciable difference in the morphology of fiber cross-sections between those fibers was observed. The difference was in the surface morphology. CPD fibers had clean surfaces and few crystallites (no crystallites for the fibers from PCS synthesized at UF; UF PCS) while CP fiber surfaces were covered with crystallites and had a porous background. After 1800°C treatment, the tensile strength of CPD fibers was retained at high levels (up to 75%) and the elastic modulus increased to a great extent (up to 35%).

7. The fractionation of silicon and SiC powders that were aged for several years was performed using a commercial dispersant, DuPont KD3 hypermer. Fractionated

silicon suspension solutions contained the particles of 0.15 μm average size and of 0.3 w/o solids content after a 7-day settling. However, KD3 hypermer did not work very well for the settling of SiC powder that was aged only for a few weeks.

8. CS fibers were prepared from PCS-based polymers with Si particles. According to Auger electron spectroscopy analysis, as-pyrolyzed CS fibers had better Si:C stoichiometry than CP fibers. CS fibers from DC PCS-SZ polymers had as-pyrolyzed tensile strength similar to that of CP fibers. However, Si particle incorporation to UF PCS resulted in a reduction of as-pyrolyzed tensile strength compared to that of CP fibers derived from UF PCS without Si particles. To obtain CS fibers of as-pyrolyzed strength greater than 2 GPa, Si particles of a smaller average size than 0.15 μm would need to be used.

9. The temperature of heat-treatments to consume Si particles incorporated for the carbothermal reduction reaction depended upon the Si content in CS fibers. A 1300°C treatment was needed for a low content (14 w/o) while a 1400°C treatment was necessary for a higher content (25 w/o). CS fibers degraded severely when heat-treated at 1500°C or higher. Porous microstructure was developed by the heat-treatments. Two mechanisms seem to be involved: a volumetric shrinkage by the carbothermal reaction between silicon and carbon, and an oxidation by surface oxide layers of Si particles. The cleaning of Si particles or CS fibers (as-pyrolyzed) using concentrated HF or HF-H₂SO₄ acid mixture did not reduce the extent of fiber degradation during heat-treatment at elevated temperatures.

10. Decaborane incorporation (CSD fibers) enhanced the thermomechanical stability of CS fibers as well. A high retention rate of tensile strength (up to 89%) after 1800°C treatment was attained. Elastic modulus of CSD fibers was as high as 293 GPa after 1800°C treatment. No apparent porosity was observed either on the surface or in the cross-section of CSD fibers treated at 1800°C. Partly due to the formation of additional SiC from incorporated Si particles, fiber density as high as 2.92 g/cm³ was attained.

11. Weibull moduli of selected fibers batches were calculated. The results showed that fibers with decaborane incorporation (CPD or CSD fibers) apparently had a greater Weibull modulus after 1800°C treatment while the Weibull modulus of CP and CS fibers decreased to some extent after 1800°C treatment. Therefore, decaborane incorporation enhanced the reliability of PCS-derived SiC fibers when they were treated at 1800°C.

12. CY fibers were processed with DC PCS-SX instead of SZ. As-pyrolyzed CY fibers did not give a good tensile strength (up to 1.0 GPa). Decaborane-incorporated CY fibers showed a good strength retention after 1800°C treatment. CX fibers were prepared from DC PCS-SZ polymers with SiC particles. Since SiC particles used were stored over years (hence they probably had been heavily oxidized), CX fibers did not show a good thermostability up to 1500°C.

CHAPTER 6

SUGGESTION/FUTURE WORK

1. The tensile strength of fibers is strongly dependent upon the defect size included in each fiber. My fibers have been processed from polymer solutions which were filtered through $0.45\ \mu\text{m}$ PTFE filters. If filters of smaller pore size, such as 0.1 or $0.2\ \mu\text{m}$, were used, tensile properties of fibers might have been better.

2. A problem with decaborane was the solubility in toluene. There was no reported data for the solubility of decaborane in toluene. One processing problem occurred when a small amount of commercial decaborane was dissolved in toluene. It made a hazy solution, which turned rather clear when the solution was filtered through a $0.45\ \mu\text{m}$ PTFE filter. It means that some portion of decaborane is not dissolved in toluene but is existing as particles of large ($\geq 0.45\ \mu\text{m}$) size so that is later screened. Therefore the actual decaborane content in the green fiber, even though the loss by filtering is believed not to be large, is not very clear. Boron is an element very difficult to measure quantitatively and more effort in this direction is needed.

3. According to TG/DTA results for decaborane addition to spinning dopes, the ceramic yield up to 1000°C slightly increased as the heating rate increases. On the other hand, the pyrolysis of preceramic polymers would become less effective as the heating rate increases. Therefore, a trade-off heating rate to optimize the effectiveness of decaborane incorporation should be found. Thus, more TG/DTA analysis needs to be

carried out.

4. Other boron precursors should to be studied for the incorporation with UF or DC PCS. Potential candidate materials are listed in Literature Survey chapter. Among them, if they are soluble in toluene, borane-amine complex materials seem to have the great possibility.

5. Even though long time aged particles (Si and α -SiC) were fractionated very well by a settling with DuPont KD3 hypermer in toluene, the newly purchased β -SiC particles and others were not settled acceptably. This was considered to be due to a difference in the oxidation state of particle surfaces. KD3 might be suitable only for surface-oxidized particles. The incorporation of fine β -SiC particles to polymers has the potential to produce SiC fibers of high modulus and good tensile strength. Therefore, there is a need for the settling study of lightly oxidized β -SiC or other particles.

6. Even though the decaborane incorporation to polymer precursors worked very well to increase the thermomechanical stability of polymer-derived SiC fibers, no fiber batches were well enough characterized to provide a good, quantitative explanation. For example, the decaborane incorporation was known to keep the fiber surface smooth even after 1800°C treatment. However, the actual boron level either on the fiber surface or in the bulk could not easily be measured. More careful and detailed characterization work needs to be performed.

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BIOGRAPHICAL SKETCH

Guang Jin Choi was born on February 23, 1959, in Inchon city, Korea. His family moved to Seoul city when he was four years old. He attended local public schools and graduated from the Youngdong High School in Seoul.

In 1981, he was awarded a Bachelor of Science in chemical engineering from the Seoul National University. He continued his academic study in chemical engineering at the Korea Advanced Institute of Science and Technology and acquired a Master of Science in 1983. Afterwards, he was working as a research scientist at the Korea Electrotechnology and Telecommunication Research Institute, located in Taejon city.

He has enrolled at the Virginia Polytechnic Institute and State University in 1986 seeking a Doctor of Philosophy degree in the materials engineering science program. He transferred to the University of Florida in 1990 to start over his graduate study for a Doctor of Philosophy in the materials science and engineering department.

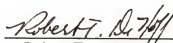
He was married to Jung Ran Kwon Choi in 1986 and they have two adorable children, Jieun and Geunsu. He is the member of Phi Kappa Phi, national honor society, American Ceramic Society, and TMS/ASM.

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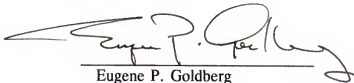
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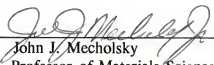
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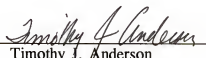


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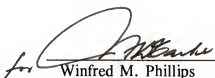

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